Journal
of the
Optical Society of America
and
Review of Scientific Instruments

Volume 18 JANUARY, 1929 Number 1

THE COORDINATION OF NORMAL AND ABNORMAL COLOR VISION

By Frank Allen, D. C. Archibald and R. A. Lind

ABSTRACT

In this communication the nervous actions underlying vision are briefly discussed. These are the conduction of the impulses from the stimulated receptors by the afferent nerves to the visual centers in the cortex, and the immediate release of enhancing and inhibiting impulses which are conducted by the efferent nerves to the retina where they control the sensitivity of the receptors.

Normal vision is the result of a perfect balance of these actions. When the enhancing actions are very weak, or the inhibitory actions strongly developed, color defectiveness or blindness results. When the enhancing activities are predominant, anomalous trichromatic vision is produced. Both varieties of abnormal vision may comprise many types according to the number of primary sensations affected.

Comparative curves of normal and both kinds of abnormal vision have been obtained by typical observers which experimentally verify these principles.

It thus becomes possible to embrace all types of color vision under one theory of nervous action.

An acceptable theory of color vision must possess a sufficiently broad and accurate group of fundamental principles to explain not only the facts of normal vision but also all variations from that type. The most commonly recognized abnormal group in vision consists of color blind persons who number about four percent of the male population, and somewhat less than 0.5 percent of the female. Another abnormal group includes those termed anomalous trichromats, the proportion of whom has not so well been determined, though it would be reasonable to suppose it was at least as large as the color blind group and possibly quite as varied in its types. Such estimates as have been made extend from about four to seven percent, probably of males. In our laboratory, investigations in color vision have been made by twelve men selected only in the sense that they have desired to enter upon re-

search work in some branch of science associated with physics. Six of these were normal in their color vision, two were color blind and four were anomalous trichromats. There seems to be, therefore, considerable reason for the belief that the last class is even larger in number than the color blind.

Insuperable difficulties have been experienced in accounting for the variations from the normal type of color vision, and much controversy has ensued between the supporters of the various theories, especially the classical theories of Young and Hering.

It has been found impossible to evade the conclusion that the principle of trichromasy in some form is fundamental in color vision. Young's theory, the first of the modern scientific hypotheses in time as well as in importance, introduced that principle and designated the primary sensations to be red, green, and violet. Some supporters of the theory, such as Helmholtz, König and Abney, modified it slightly by the substitution of blue for violet; and several have also assumed an additional sensation of white. The rival theory of Hering is based upon the assumption of the existence of three photo-chemical substances in the retina, in which the opposing processes of dissimilation and assimilation are induced by the action of the corresponding pairs of color or light stimuli, red-green, yellow-blue, and white-black.

The authors of these, as well as of the three or four score additional theories by which the subject of color vision has unfortunately become so complicated, in all cases assumed that vision involved only a single process of afferent nervous action. It was supposed that after excitation of the receptors by waves of light, impulses were conducted from them to the cortical visual centers where they evoked the appropriate sensations of color, and that this process completed the very simple series of neural activities associated with vision.

Abundant experimental evidence of the most direct character has been adduced by Allen[1] to prove that these primary sensations, red, green, and violet, have a definite existence. The same investigations have also shown that stimulation of the retina by all colors evokes sensory reflex actions in the visual nervous mechanism which either enhance or inhibit the responsiveness of the retinal receptors whose sensitivity they thus control.

The mechanism of vision, as far as we can ascertain it at present, possesses the following characteristics. The retina contains visual

[1] J.O.S.A. & R.S.I., 7, p. 583 and p. 913; 1923.

receptors—the rods and cones—which are stimulated by light in three elementary modes, corresponding to the same number of primary sensations in the cortex. Excitation of the receptors by any adequate wave stimulus initiates impulses in the afferent nerves by which the three primary sensations in the cortical visual centers are evoked to unequal degrees, and also in unequal times which are too small to be ordinarily perceptible. Thus a color is never seen by itself in perfect purity and saturation. In addition to the direct actions, reflex nervous impulses are elicited which are carried by efferent nerves from the cortex to the retina, where they exercise the highly important function of controlling the sensitivity of the visual apparatus. The precise nature of these neural reflexes has not yet been fully determined, and Parsons[2] has suggested the possibility that they are of the type called axon reflexes which do not require efferent nerves. It is important to observe that the control of receptor responsiveness is accomplished by two opposing nervous functions, one which causes enhancement and the other depression of sensitivity.

As the sensory reactions have only recently become known, all theories of color vision have necessarily been formulated in ignorance of their existence. Since their functions are so important it is not surprising that formidable difficulties have invariably arisen in such explanations of many of the facts of vision as could be given by any theory. In place of a single group of actions to be taken into account there are now known to be three; but instead of complicating the subject still further the unravelling of the complex fabric of chromatic vision is thereby immensely facilitated.

In the present paper there is proposed a coördination of the abnormal types of color perception with the normal characteristics of vision founded upon the three modes of nervous response.

The method[3] of investigation is that known as the measurement of the persistence of vision or the critical frequency of flicker. The source of spectral light of the necessary invariable physical intensity was an acetylene flame for which the gas was supplied at a constant pressure. In the earlier investigations the spectrometer possessed two, and in the present study three, sixty degree prisms which consequently gave spectra of considerable dispersion. With a shutter eye-piece a small rectangular band of any desired color was isolated, and its critical fre-

[2] The Theory of Perception, p. 222; 1927.

[3] See papers by Allen previously cited.

quency of flicker computed from chronographic records of the speed of the rotating sectored disk and the rate of a clock.

Some years ago one of the writers (Allen) investigated[4] by this method a group of twenty-three color blind subjects. Previous to this Ferry[5] had also applied the method to study the vision of three such persons. Persistency curves were thus obtained for a group of color blind subjects sufficiently large to afford a fairly reliable basis of classi-

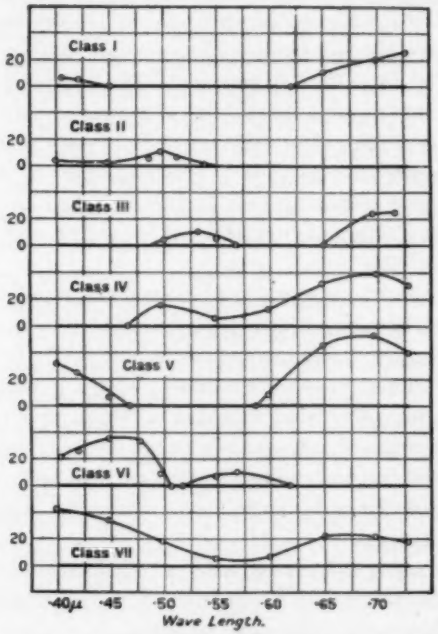

FIG. 1. *Reduced persistency curves for color defective subjects. Class I, red defective. Class II, green defective. Classes III and IV, red-green defective. Class V, red-violet defective. Class VI, green-violet defective. Class VII, totally color defective. In each case normal vision is represented by a horizontal straight line.*

fication. In all cases the results conformed to the provisions of the Young theory.

According to this theory seven classes of color blindness are possible: first, three classes comprising those who are defective in one of the three sensations, red, green or violet; second, three classes of subjects

[4] Phys. Rev., *15*, p. 193; 1902.
[5] Am. Jour. Sci., *44*, 1892.

who are defective in two sensations, red-green, red-violet or green-violet; third, a single class of subjects who are defective in all three sensations, and who in consequence are totally color blind. Of these seven types six were found in the group referred to, the missing class being the violet blind. The largest classes were those defective in the red-green and red-violet sensations. Only one case was found to be defective in the green-violet combination, and only a single case of complete color blindness.

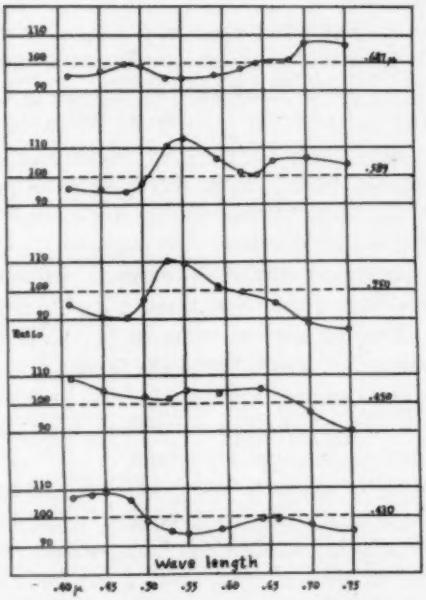

FIG. 2. *Reduced persistency curves for eye stimulated with colors indicated at the right-hand margin. Normal vision is represented by horizontal broken line.*

Reduced persistency curves representative of these classes are here reproduced in Fig 1. In every case the normal curve of the color blind subject is elevated above the comparison normal of Allen which is represented by a straight horizontal line. The eyes of all observers were in daylight adaptation when the measurements were made. From this figure it is clear that the elevations of the curves of color blind subjects above the comparison curve of an observer with normal color vision

[6] J.O.S.A. & R.S.I., 7, p. 583; 1923.

in all cases correspond to the red, green and violet parts of the spectrum and thus can be classified in accordance with the trichromatic theory of Young.

When a person with normal color vision stimulates[6] his observing eye with red, green or violet spectral colors, his presistency curves are similarly elevated above the normal in the corresponding portions as shown in Fig. 2. When the stimulus is any compound color, such as orange, yellow or blue, two sensations instead of one are affected and consequently two elevations are produced. The sensations not directly excited are enhanced in responsiveness as is shown in the lowered position beneath the normal of the corresponding parts of the curve. Thus, when the stimulus is yellow light, elevations occur in the red and green regions, while the violet portion is lowered. When the stimulus is blue light, the elevations occur in the green and violet regions and the lowered portion corresponds to red. As the physical intensity of the spectrum remains constant, the elevations denote a diminished physiological brightness of the colors in question. The receptors are therefore reduced to a state of diminished sensitivity which is selective in character.

Extensive series of measurements through a wide range of intensities of stimulation either of the observing or of the non-observing eye, prove that the depressed sensitivity in the former case may, and in the latter must be due to sensory reflex action of the inhibitory type. The Fechner Effect, the so-called Fechner Paradox, is a familiar example of this type of sensory reaction involving both eyes.

Reflex actions of the opposite type, which selectively enhance the sensitivity of the retinal receptors have also been discovered. These effects are graphically indicated in Fig. 3 by portions of the persistency curves being lowered beneath the normal, a condition which is due to an augmented physiological brightness of the corresponding parts of the spectrum. This indicates an enhanced degree of sensitivity of the receptors. As is the case with the elevations, the lowered portions are also invariably found to correspond with the red, green, and violet colors. These experimental results sufficiently attest the truth of the Young theory of color vision in so far as it involves the selection of three fundamental sensations corresponding to the colors named. They also prove the existence of opponent actions in the visual nerves which, in the assumption of opponent colors, is one of the chief provisions of the Hering theory. The two theories are thus in a considerable degree reconciled.

In an investigation of anomalous trichromatic vision in this laboratory, Anderson[7] obtained the normal persistency curve for his own eye which is shown in Fig. 4. As there was no curve representative of normal color vision with which to compare it, the peculiar elevation of the curve in the orange between the wave lengths .59μ and .66μ was assumed to indicate the region of his anomaly. On this assumption the numerous experimental curves were interpreted. The curve itself was doubly anomalous since an elevation in any part of the curve other

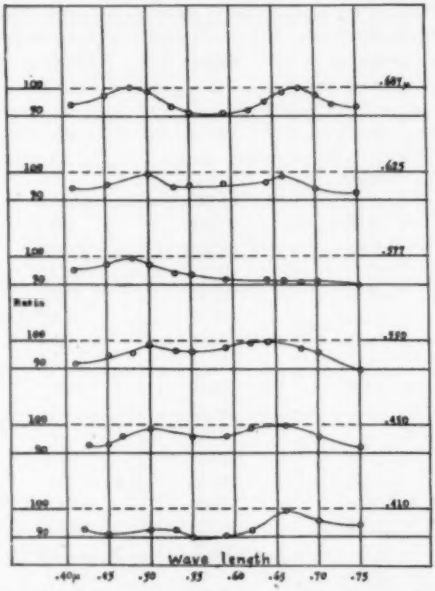

FIG. 3. *Reduced persistency curves for right eye when left eye was stimulated by colors indicated in margin. Normal vision indicated by horizontal broken line.*

than those corresponding to red, green, and violet had never before been obtained. This strange occurrence often became a matter for reflection and the idea gradually formed that the curve was not elevated in the orange at all, but that it was lowered in the regions, red and green, on either side. From this new point of view the curve was interpreted to mean that in anomalous trichromatic vision either the red or the green, or both sensations were in a condition of supersensitivity, whereas in color blindness the sensations were subsensitive, the sensi-

[7] J.O.S.A. & R.S.I., *8*, p. 731; 1924.

tivity of the normal eye being taken as the standard of comparision.

In addition to Anderson's curve there are shown in Figs. 5 and 6, from the measurements in Table 1, the curves of three other observers, Blair, Fleming and Smith, which have been obtained in our laboratory, but which have not hitherto been published. They all show the same peculiarities of anomalous trichromatism which are discussed in this investigation. The type of curve, therefore, is characteristic of anomalous vision.

TABLE 1. *Normal persistency curves for anomalous vision.*

λ	Anderson D	Blair D	Fleming D	Smith D
	sec.	sec.	sec.	sec.
.75μ	0.0335	—	—	—
.74	.0309	0.0341	0.0269	0.0260
.72	.0256	.0283	.0242	.0210
.70	.0206	.0225	.0204	.0177
.68	.0171	.0179	.0175	.0152
.66	.0153	.0156	.0167	.0145
.64	.0148	.0152	.0162	.0140
.62	.0138	.0141	.0149	.0127
.61	—	.0135	—	—
.59	.0125	.0123	.0128	.0107
.58	—	.0122	—	—
.57	—	.0123	—	—
.55	.0130	.0124	.0135	.0120
.53	.0141	.0130	.0143	.0130
.50	.0166	.0147	.0176	.0160
.48	.0200	.0180	.0212	.0190
.46	—	.0229	.0250	.0235
.45	.0276	—	—	—
.44	.0307	.0280	.0315	.0290
.42	.0396	.0373	.0359	.0360

By a most unexpected and fortunate coincidence three young men of about the same age and of different types of color vision were recently in this laboratory at the same time. All of them obtained persistency curves under identical conditions so that they are strictly comparable. One of the three was known to be color blind; and of the remaining two, who are joint authors of this paper, one possessed normal and the other, as his curve indicated, anomalous vision. The curves are shown together in Fig. 7, and the measurements are given in Table 2. In the lower part of the figure the curves are drawn in another form. The curve

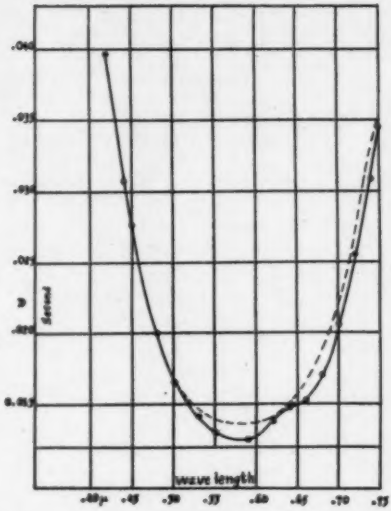

FIG. 4. *Persistency curve indicating anomalous vision. Anderson. Hypothetical normal is indicated by broken line.*

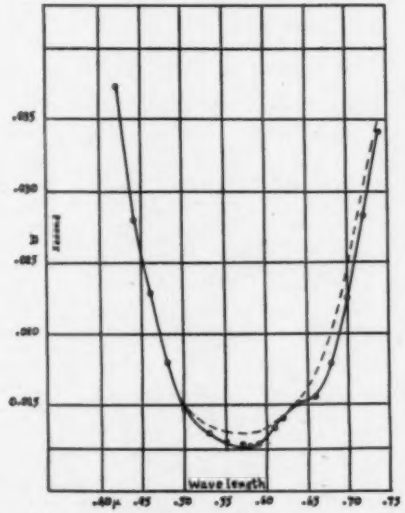

FIG. 5. *Persistency curve indicating anomalous vision. Blair. Hypothetical normal is indicated by broken line.*

for normal vision (Lind) is everywhere given an arbitrary value of 100 and the others are proportionally reduced. By this method the divergences of the curves of abnormal vision from that for normal can, be more readily seen.

It was shown by Ferry[8], and confirmed by Allen[9], that people whose ages were about the same, or not widely different, obtained identical curves when their vision was normal. In all forms of abnormal vision except total color blindness, which have been examined by this method

TABLE 2. *Normal persistency curves.*

λ	Normal vision R.A.L.	Reduced	Anomalous vision D.C.A.	Reduced	Color-blind subject	Reduced
	D sec.		D sec.		D sec.	
.74μ	0.0219	100	0.0212	97	0.0237	108
.72	.0200	100	.0189	94	.0218	109
.70	.0180	100	.0171	95	.0196	109
.68	.0168	100	.0154	92	—	—
.66	.0152	100	.0146	96	—	—
.64	.0142	100	.0142	100	.0145	102
.63	—	—	.0136	99	—	—
.62	.0132	100	.0130	98.5	.0131	99
.61	—	—	.0121	96	—	—
.59	.0123	100	.0116	94	.0128	104
.55	.0129	100	.0120	93	.0137	106
.53	.0137	100	.0130	95	.0142	104
.50	.0160	100	.0156	97.5	.0174	109
.48	.0184	100	.0185	101	.0214	116
.46	.0209	100	.0207	99	.0263	126
.44	.0240	100	.0243	101	.0291	121
.42	.0285	100	.0284	100	.0329	121

some part of the curve always coincided with that of a normal observer obtained under the same conditions. In the present case, therefore, the coincidences and divergences of the three curves are not accidental but are characteristic of the respective types of vision.

Examination of these curves in Fig. 7 reveals a very simple relationship between them. The curve, *A*, for the color blind subject is decidedly elevated at both ends of the spectrum and therefore proves him to be of the numerous class of red-violet defectives. In this case the

[8] Op. Cit.

[9] Phys. Rev., *15*, p. 196; 1902.

green sensation also appears to be slightly defective. This would indicate that to some extent his vision approximates total color blindness.

The curve, *C*, for the anomalous trichromatic subject is of remarkable interest since it practically coincides with the normal, *B*, throughout the violet and blue to the wave length .50μ, then passes below it for the remainder of its course except where they meet again at the wave length .64μ, in the orange.

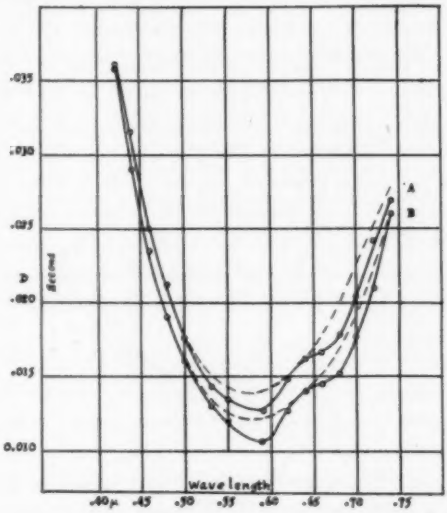

FIG. 6. *Persistency curves for anomalous vision. A, Fleming. B, Smith. Hypothetical normal is indicated by broken lines.*

These characteristics of the curves indicate that the violet sensation of the anomalous subject is normal in its behavior and that the red and green sensations, especially the latter, are much enhanced in sensitivity. The anticipated supersensitivity of the red and green sensations is thus verified.

The relationship of abnormal to normal color vision may now be formulated more completely than has hitherto been possible. In the nervous visual mechanism of the normal eye there is maintained an exquisite balance between the direct effect of stimulation and the reflex actions of enhancement and inhibition by which the sensitivity is controlled. In color blindness the direct effects of stimulation are con-

siderably reduced in intensity because the reflex process of inhibition is for some reason much more prominently developed than the enhancing action, or else the latter is greatly underdeveloped. In anomalous trichromatism the opposite condition prevails. The enhancing actions are far more highly developed than the inhibitory. Color blindness, therefore, is due primarily to the predominance of inhibitory and anomalous vision of enhancing processes, which in both types may apply to any one, or two, or all three sensations. It is quite possible, conse-

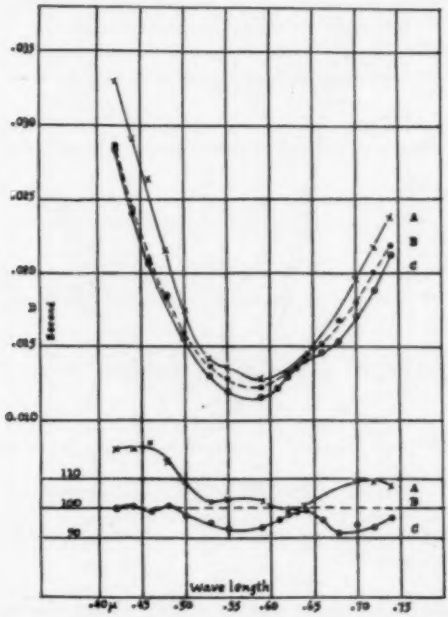

FIG. 7. *Persistency curves for three types of vision: A, color blind; B, normal; C, anomalous vision.*

quently, that as many types of anomalous vision may be discovered as there are forms of color blindness.

To this theory it will at once be objected that color blindness cannot be due only to partial or total inhibition of receptor sensitivity, since colors within the range of defective vision are seen not only less bright than normal but as quite different hues. Unfortunately persons with normal vision cannot form a correct conception of the appearance of colors to the color blind. We cannot experience each other's sensations.

In mild cases of color blindness that have been examined in this laboratory there was apparently some degree of correct appreciation of all colors under suitable conditions of intensity. We are consequently not in a position to realize just what modifications of color perception a strong degree of inhibition will produce.

The experiments of Burch[10] on the effects of very intense stimulation with different colors probably give some idea of the influence of strong inhibitory action on the sensations. Thus after stimulation by red light, the red end of the spectrum is shortened and the green sensation extends through the yellow almost as far as the wave length .656μ, which in normal vision is bright red. After stimulation by green that color disappears from the spectrum and is replaced by red and blue which may even overlap. It is to be expected, therefore, that the presence of strongly predominant inhibition in one or more of the primary receptor actions will be accompanied by a radically different reconstruction of the color scheme to a degree depending on the range and intensity of the inhibition. If, in addition, the nervous actions permit equality of stimulation of the red and green sensations by all the longer wave lengths of the spectrum, all those colors will tend to be perceived as yellow.

It may be remarked in passing that temporary color blindness caused by the excessive use of strong narcotics is probably due to prolonged and intense degrees of inhibition induced by those powerful drugs.

There is some reason for the belief that negative after-images are due to the enhancing nervous actions. In two of the cases of color blindness that have been examined here, one of whom, Hollenberg,[11] has published an investigation of his own vision, after-images had never been experienced and were therefore unknown. This was not through neglect of observation since both persons had endeavored to obtain them under the instruction of one of the writers. Hollenberg found a notable absence of enchancing actions in his eye under the same experimental conditions that brought them into prominence in the normal eye.

It is known that light of every wave length invariably excites the three fundamental sensations, though usually in unequal amounts. In this way our normal color perceptions are formed. Red light, for example, excites the red sensation to the greatest degree and green and

[10] Parsons, Colour Vision, 2nd Ed. p. 125.
[11] J.O.S.A. & R.S.I., *9*, p. 389; 1924.

violet to lesser extents. If now, the red sensation is strongly inhibited, the perception must be limited to the undisturbed sensations of green and violet. What is perceived, therefore, must be a mixture of green and violet together with what little amount of the red sensation remains. In such a combination the green sensation will predominate, but it will not be pure. The inhibition of the red of necessity will lower the brightness of the red end of the spectrum and because of the diminished brightness reduced its extent. As the violet fundamental sensation[12] has a slight admixture of red, which is more luminous than the underlying blue, the violet end of the spectrum may likewise become shortened. It is not necessary, therefore, to assume that in red color blindness the red sensation does not exist, but only that it is inhibited from action in various degrees.

Cases are known, probably pathological in character, in which temporary color blindness has occurred for considerable periods of time after which they recover their normal vision completely. In such cases it is impossible that one or more color sensations should cease to exist for a time and then revive; but it is easily possible that some cause might temporarily block the enchancing nervous actions and leave only the inhibitory impulses to interfere with the normal vision of colors. When the enhancing actions recover their ordinary power the normal operations of the color sensations is re-established. Quite possibly if some way of artificially stimulating the defective nerves at their cortical centers could be discovered, congenital color blindness might be cured.

All the evidence at present available, therefore, converges upon the theory that color blindness or color defectiveness is at least in large measure caused by excessive development of the inhibitory reactions in the visual nervous mechanism by which the receptors involved are permanently depressed in sensitivity.

The peculiarities of anomalous trichromatic vision are by no means so well-known as those of color blindness. Probably there is not so much to be known, as the effects of enchancement or supersensitivity seem to cause far less disturbance of the color system than is found in the subsensitive state induced by inhibition. The color sensations are normal in appearance as far as hue is concerned, but the degrees to which they are evoked are different. Our knowledge of the peculiarities of this type of abnormal vision is largely confined to those who, in

[12] Allen and Fleming, Phil. Mag., *6*, p. 337; 1928.

matching spectral yellow by mixtures of red and green colors, require different proportions of these colors than normal subjects. In some cases the red sensation is supersensitive, in others the green.

Anderson, in the investigation cited, found his red sensation was so readily enhanced that after 30 seconds fixation a bright white light assumed for a time a pink hue. Also when a brilliant green color was fixated for 25 seconds it became more purple than green, increasing in saturation for the same length of time, then decreasing until, in 90 seconds, the green color was restored but much reduced in intensity and saturation. The red color, however, never changed its hue under any conditions.

These experimental facts are all in accordance with the view that anomalous trichromatic vision is the result of predominant action of the enhancing influence in the nervous mechanism, by which some of the receptors are maintained in a state of supersensitivity.

In a discussion of this subject by von Kries[13] it is stated that in extreme cases of green anomaly the power of discrimination between the green and yellow colors extending from the wave lengths .535μ, to .570μ, is so much diminished that they look approximately the same. Likewise in extreme cases of red anomaly the yellow and orange colors appear to be much the same as red. These characteristics seem to be quite in accord with the explanation of anomalous vision which we are advancing. For extreme enchancement of the green or red sensations would easily extend the perception of those colors through much greater regions of the spectrum than is found in normal vision. Thus in the two types of vision there would be unusual extension of either the red or the green color, and consequently the transition from one or the other of them to yellow would be more abrupt.

It is also stated by von Kries that Nagel found certain contrast phenomena were accentuated in anomalous subjects. "For example, a yellow field viewed by itself is described correctly as yellow; but if it is displayed alongside a red field, it is then called green. This is the explanation of what is practically a very important fact, namely, that in observing two adjacent objects of different colors, anomalous persons are liable to make big mistakes that would be entirely out of the question in normal vision. Thus a gas light or electric light of the usual pale yellow color is taken for green if it is put by the side of a red light."

[13] Helmholtz, Physiological Optics. English Trans., *2*, pp. 410 and 411.

These facts again are conformable with the present theory. For it is known[14] that by reflex action stimulated retinal areas act inductively upon each other in such a way that each color enhances predominantly the sensations complementary to itself. A red color, therefore, would enhance the green sensation in an adjoining area so that yellow light falling upon it would acquire a greenish hue. This is true in normal vision and it is undoubtedly the cause of simultaneous color contrast. In anomalous vision where, for example, the green sensation is enhanced with extraordinary ease, the contrast effect would be, as Nagel states, much accentuated.

The conclusions to which we have come in this paper may be briefly summarised. In the bulk of humanity there seems to be preserved a proper balance between the direct results of sensory stimulation and the reflex actions which are evoked. This condition is termed normal vision. Some four percent of men have this balance broken by over development of inhibition. They are accordingly selectively subsensitive in their defective color sensations. Another proportion possibly as high as six or seven percent, have the normal balance disturbed in the opposite direction by over development of the enhancing actions. Such persons, therefore, possess supersensitive color vision, which is likewise selective in regard to the precise sensations affected.

Probably a similar grouping of people can be made in regard to every sense organ. The great majority are normal, and smaller groups are either subsensitive or supersensitive. Possibly this principle may be generalized to cover the intellectual powers of the mind, and the emotional and volitional faculties as well. For in all these divisions the normal, the super-normal and the sub-normal groups are well recognized. Thus the principle at which we have arrived from experiments on vision may have in the broad field of psychology the widest application.

This investigation forms part of a series of researches in Color Vision conducted under the direction of Professor Frank Allen with the assistance of the National Research Council of Canada, to whom we desire to express our thanks.

DEPARTMENT OF PHYSICS,
UNIVERSITY OF MANITOBA,
WINNIPEG, CANADA, JULY, 1928.

[14] Allen, On Reflex Visual Sensations and Color Contrast. J.O.S.A. & R.S.I., 7, p. 913; 1923.

LUMINESCENCE ASSOCIATED WITH ELECTROLYSIS

By R. T. Dufford

The luminescence which occurs at the anode of a Nodon valve has been described by Lemon,[1] who showed that the brightness increased with the voltage applied, and that the spectrum is essentially continuous (it covers the whole visible range except at the red end). Similar luminescence has been found[2] in anhydrous ether solutions of many Grignard reagents (organo-magnesium halides); these gave the effect with every metal tested as electrodes.

It seemed to the writer to be desirable to learn more concerning these phenomena. Studies were accordingly made of several aspects of the question, such as (a) to discover how widespread the effect is, (b) to measure the brightness of the luminescence, (c) to determine the efficiency of the process, and (d) to find how the brightness and the efficiency are affected by changes in the applied voltage, in concentration, in the nature of the solution, and by impurities.

The occurrence of this type of luminescence is fairly frequent. Thus, for example, with aluminum as anode, the effect was found in aqueous solutions of no less than twenty-five different substances, mostly of neutral salts or bases, though phosphoric acid is an exception. No doubt this number could be increased readily, for it is not intended to imply that the accompanying list is complete; it gives enough typical substances to show what to expect from similar compounds. The most interesting substances (with aluminum anodes) are the sodium phosphates and carbonates. Similarly, from one to eight solutions each were found which gave some light, usually very faint, with zinc, silver, magnesium, cerium (mischmetall), antimony, mercury, tantalum, and tungsten. The results are summarized in Table 1. Apparently the effect is a fairly regular accompaniment of the more pronounced cases of what is known as mechanical passivity. None of the aqueous solutions studied gave any light with lead, iron, copper, tin, nickel, molybdenum, or platinum. In some cases, the light obtained occurs only as scintillations; in others, there is a continuous glow in addition; in the cases studied more fully below, the steady glow was observed, the scintillations being either relatively unimportant or entirely absent.

[1] H. B. Lemon, Science, *47*, p. 170; 1918.

[2] Dufford, Nightingale, and Gaddum, J. Am. Chem. Soc., *49*, p. 1858; 1927.

TABLE 1.

Substances found to give luminescence during electrolysis of their aqueous solutions.

With aluminum: Mono-, di-, and tri-sodium phosphates; sodium pyrophosphate; phosphoric acid; ammonium phosphate; calcium phosphate; sodium bicarbonate; sodium, potassium, and calcium carbonates; sodium sulphite; sodium sulphate; ammonium sulphate; potassium permanganate; sodium nitrite; sodium borate; sodium hydroxide; sodium oleate; sodium, lead, and zinc acetates; sodium and sodium-potassium tartrates; sodium citrate; sodium oxalate; potassium dichromate.

With zinc: sodium hydroxide.

With silver: ammonium sulphate, potassium dichromate.

With tantalum: sodium bicarbonate, sulphite, nitrate, nitrite, hydroxide, and oxalate; ammonium sulphate; sulphuric acid; pyrogallol.

With tungsten: sodium bicarbonate, chloride, nitrate, nitrite, and oxalate; ammonium sulphate; potassium chlorate; potassium dichromate; pyrogallol.

With magnesium: di-sodium phosphate; sodium hydroxide and oxalate.

With cerium (mischmetall): sodium bicarbonate and sulphite.

With antimony: di-sodium phosphate; sodium bicarbonate, sulphite, and hydroxide; ammonium sulphate; potassium dichromate; pyrogallol.

With mercury: di-sodium phosphate; ammonium sulphate; sodium bicarbonate and chloride; hydrochloric acid.

Metals giving no luminescence: lead, iron, copper, nickel, molybdenum, tin, platinum.

The name electroluminescence naturally suggests itself for a luminescence produced in this way; but unfortunately this term, along with anodoluminescence and cathodoluminescence, has been appropriated for the description of the effects observed in the discharge through gases. It is not clear that the present effect should be classified as chemiluminescence, though of course there must be chemical reactions which accompany the electrolysis. Another name would be useful.

In order to state the essentials as briefly as possible, the phenomena with aluminum anodes in aqueous solutions will be described first; the discussion will apply in a general way to all the other cases, so that it will be necessary to mention only the modifications which apply to particular cases, such as the non-aqueous solutions of Grignard compounds.

While the nature of the processes giving rise to the radiation is not entirely understood, it may be stated in general that the light is given out by a film which covers the electrode, and which apparently is responsible for the ability of the electrode to act as a rectifier. The electrical resistance of such a film is generally very high; for example, in a cell with one electrode of aluminum, the other of lead (any other of the electrodes listed as giving no light might have replaced the lead), the resistance of the cell when the aluminum was the anode was 35,000 ohms, while when the current was reversed the resistance was 12 ohms.

The latter figure should give approximately the resistance of the cell solution, and the difference is the resistance of the film on the anode. These figures are for one typical cell; other cells with aluminum anodes gave resistances from a few thousand up to 5×10^6 ohms. It follows that when such a film is fully formed, more than 99% of the applied voltage is used in driving current through the film. That the effect is really due to the film can be shown in several ways. The film can be punctured mechanically, by scratching the electrode; if this be done while a voltage sufficient to cause emission of light is applied, the current increases suddenly, accompanied by a flash at the point of puncture. The film re-forms quickly, however, causing the current and the emission of light to decrease. If the electrode becomes heated, so that the solution begins to boil, the bubbles continually puncture the film, and prevent the use of the cell as a rectifier. The film on aluminum is immediately destroyed by the addition of a little hydrochloric, nitric, or sulphuric acid. It is destroyed very quickly by reversing the current. Because of this, and the fact that it requires an appreciable time to re-form the film, such a cell never reaches its full resistance when used to rectify 60-cycle alternating current. By increasing the voltage slowly, it is possible to apply voltages safely that, if applied suddenly before the film is formed, would overheat the anode and boil the solution thus preventing the formation of the film. The destruction of such films by high temperature, with consequent loss of ability to rectify alternating current, is well known.[3]

If a fresh aluminum electrode is used, not covered by a film, the application of an emf will give a rush of current that will die down in a few hundredths of a second to a few milliamperes, and then will change relatively slowly with time. The light emitted is correspondingly bright at first, but dims rapidly, and after a few seconds the change is relatively slow; so that while its value is not perfectly constant, it is nearly enough so to make it possible to obtain fairly consistent readings of the brightness. In the discussion of brightness and efficiency below, such steady-state readings are referred to unless the contrary is specifically stated. However, since the brightness does change with time, and with other variables even more, it is of course impossible for such readings to give more than a good idea of the order of magnitude of the effect; but even such results serve in the present case to bring out

[3] Fischer, ZS. Elektrochem., *10*, p. 869; 1904; also Thompson, Theoretical and Applied Electrochemistry, pp. 138–143; 1925 Ed.

facts of considerable interest. With small electrodes in relatively large vessels, the brightness is surprisingly uniform over the entire surface of the electrode.

With aluminum anodes, the light becomes visible usually somewhere in the range 40 to 90 volts; as the voltage is increased above this value, the increase in brightness is extremely rapid for the next hundred volts or so. But further increase in voltage gives a less and less rapid increase in brightness, and even a decrease if sufficiently high voltages can be used. Results for a few selected runs, typical of a large number obtained, are shown in the accompanying figures. The brightness corresponding to the threshold of visibility, under the conditions of the experiments, was found to be about 6.7×10^{-9} lamberts, for three observers. The ratio of highest to lowest brightnesses observed was between one and ten thousand. The measurements depend on a curve of relative candlepower as a function of applied voltage, for a standard 25-watt lamp; the writer is indebted to Mr. A. H. Taylor, of the Lighting Research Laboratory, for this curve. Brightnesses below 1.6×10^{-8} lamberts depend on an extrapolation of this curve from 10 to 8 volts; but the smoothness of the curve from 100 to 10 volts makes it seem improbable that any error due to extrapolation would be as large as the actual variations due to such causes as temperature changes.

The product of brightness in lamberts and the area of the electrode emitting the light, gives the number of lumens being emitted. If the usual value of 640 lumens to the watt is used, the power emitted as light can be obtained. The ratio of the power emitted to the electrical power input gives that which for practical purposes is the efficiency of the process; this neglects possible contributions of energy from chemical reactions, but it is probable that any such contributions are negligible. In a large number of determinations of efficiency, the values all lie in the range from 10^{-8} to 5×10^{-6}%. These disappointingly low values are, however, in fair agreement with the few determinations published for other similar cases of luminescence; e.g., 1.7×10^{-4}% for the oxidation of phosphorus, obtained by Adams,[4] and a tentative, not previously published value of 1.7×10^{-7}% for the oxidation of pyrogallol, also obtained by Adams, who has kindly given the writer permission to mention this result. Harvey[5] finds a higher value of 0.156% for certain

[4] E. Q. Adams, Phys. Rev., *23*, p. 771; 1924; Bull. Natl. Res. Council, no. 59, p. 39; 1927.

[5] E. N. Harvey, J. Gen. Physiol., *8*, p. 89; 1925; Bull. Natl. Res. Council, no. 59, p. 39; 1927.

TABLE 2. *Typical values of brightness and efficiency for luminescence during electrolysis.*

A. Aluminum anodes, in aqueous solutions.

Solute	Concentration	Elec. volts	Input watts	Electrode area	Brightness (lamberts)	Efficiency (per cent)
$NaHCO_3$	5%	88	0.888	9.49 cm²	6.7×10^{-9}	1.1×10^{-7}
		110	.440		2.7×10^{-7}	9.1×10^{-7}
		150	.900		1.9×10^{-6}	3.1×10^{-6}
		200	4.00		7.8×10^{-6}	2.9×10^{-6}
		*250	15.0		1.6×10^{-5}	1.5×10^{-6}*
		*300	.60		2.3×10^{-7}	5.7×10^{-7}*
$NaHCO_3$	1%	88	.616	9.49 "	6.7×10^{-9}	1.6×10^{-6}
		110	5.50		2.8×10^{-7}	7.6×10^{-6}
		*150	1.80		5.2×10^{-5}	4.3×10^{-5}*
		*200	8.20		3.3×10^{-7}	6.0×10^{-5}*
		*250	155.		1.6×10^{-6}	1.5×10^{-5}*
$NaHCO_3$	10%	84	.084	9.49 "	6.7×10^{-9}	1.2×10^{-7}
		102	.408		4.2×10^{-8}	1.5×10^{-7}
		150	1.50		1.7×10^{-6}	1.7×10^{-6}
		*200	1.00		3.1×10^{-6}	4.6×10^{-6}*
H_3PO_4	1%	52	.052	8.96 "	6.7×10^{-9}	1.8×10^{-7}
		95	9.50		1.2×10^{-6}	1.8×10^{-7}
		*150	165.		4.6×10^{-6}	4.6×10^{-5}*
NaH_2PO_4	5%	46	.230	8.96 "	6.7×10^{-9}	3.9×10^{-8}
		70	1.54		5.2×10^{-8}	4.7×10^{-8}
		111	6.88		1.3×10^{-6}	2.7×10^{-7}
		150	30.0		3.5×10^{-6}	1.6×10^{-7}
		*200	110		5.7×10^{-6}	7.3×10^{-5}*
		*250	188.		3.14×10^{-6}	2.3×10^{-5}*
NaH_2PO_4 +.05% NaOH	5%	46	.230	8.96 "	6.7×10^{-9}	3.9×10^{-8}
		60	.840		9.6×10^{-8}	1.6×10^{-7}
		111	6.22		1.0×10^{-6}	2.3×10^{-7}
		150	24.0		3.8×10^{-6}	2.2×10^{-7}
		*200	10.0		8.1×10^{-6}	1.1×10^{-6}*
Na_2HPO_4	5%	84	.336	9.49 "	6.7×10^{-9}	3.0×10^{-8}
		112	.896		5.4×10^{-7}	8.9×10^{-7}
		*150	30.0		7.0×10^{-6}	3.5×10^{-7}*
Na_2HPO_4 +0.6% NaOH	5%	41	.082	9.35 "	6.7×10^{-9}	1.2×10^{-7}
		102	2.65		6.0×10^{-7}	3.3×10^{-7}
		150	9.00		3.5×10^{-6}	5.6×10^{-7}
		*200	20.0		1.1×10^{-5}	7.7×10^{-7}*
		*250	88.0		2.5×10^{-5}	4.2×10^{-7}*
Na_3PO_4	1%	35	.245	8.96 "	6.7×10^{-9}	3.8×10^{-8}
		60	1.20		5.2×10^{-8}	6.1×10^{-8}
		114	5.70		2.4×10^{-6}	5.9×10^{-7}
		150	45.0		8.8×10^{-6}	2.7×10^{-7}
		*200	80.0		3.2×10^{-5}	5.6×10^{-7}*

* "Flash reading."

TABLE 2. (continued)

Solute	Concentration	Elec. volts	Input watts	Electrode area	Brightness (lamberts)	Efficiency (per cent)
Na_3PO_4 +.05% NaOH	1%	25	.050	8.96 cm²	6.7×10^{-9}	1.87×10^{-7}
		60	.480		8.8×10^{-8}	2.6×10^{-7}
		113	2.26		2.1×10^{-6}	1.2×10^{-6}
		150	6.00		1.2×10^{-5}	2.8×10^{-6}
		*200	22.0		2.5×10^{-5}	1.6×10^{-6}*
		*250	67.5		3.8×10^{-5}	7.9×10^{-7}*
$Na_2P_4O_7$ +0.2% NaOH	5%	29	.058	9.35 "	6.7×10^{-9}	1.7×10^{-7}
		103	5.15		1.7×10^{-6}	4.8×10^{-7}
		150	16.5		9.4×10^{-6}	8.3×10^{-7}
		200	34.0		2.0×10^{-5}	8.6×10^{-7}
		*250	92.7		6.0×10^{-5}	9.5×10^{-7}*
$Na_2B_4O_7$	10%	107	.535	12.5 "	3.6×10^{-7}	1.3×10^{-6}
B. Tantalum anode, in aqueous solution						
$NaNO_3$	5%	150	2.25	10.1 cm²	2.1×10^{-7}	9.8×10^{-8}
		*200	4.00		6.3×10^{-6}	2.5×10^{-6}*
C. Platinum electrode, in anhydrous ether solution						
C_6H_5MgBr	2M	110	1.87	2.4 cm²	1.1×10^{-6}	2.2×10^{-7}
		150	4.50		1.7×10^{-6}	1.4×10^{-7}
		200	8.00		2.4×10^{-6}	1.1×10^{-7}
		250	12.5		2.7×10^{-6}	8.1×10^{-8}
		*300	18.0		4.6×10^{-6}	9.6×10^{-8}*
$p-BrC_6H_4MgBr$	a†	40	.040	2.4 "	6.7×10^{-9}	6.3×10^{-8}
		106	.636		7.4×10^{-7}	4.4×10^{-7}
		200	2.00		8.8×10^{-7}	1.7×10^{-7}
		*300	3.00		5.4×10^{-6}	6.7×10^{-7}*
$p-BrC_6H_4MgBr$	b†	150	.750	2.4 "	8.0×10^{-7}	4.0×10^{-7}
		200	1.40		9.4×10^{-7}	2.5×10^{-7}
		250	2.00		1.9×10^{-6}	3.6×10^{-7}
		300	3.00		2.7×10^{-6}	3.3×10^{-7}
		350	5.25		4.6×10^{-6}	3.3×10^{-7}
		400	6.00		4.4×10^{-6}	2.8×10^{-7}
		450	6.75		3.5×10^{-6}	1.9×10^{-7}
		*500	7.50		6.6×10^{-6}	3.3×10^{-7}*
		*600	10.2		1.4×10^{-5}	5.0×10^{-7}*
		*700	14.0		2.0×10^{-5}	5.4×10^{-7}*

[a] lower layer, [b] upper layer, of a solution made up to 1M strength.
† Light from cathode.

luminous bacteria; a few other less nearly related determinations are quoted in the reference last given.

Curves showing the change in efficiency with change in voltage are shown along with the brightness curves in the accompanying figures. Each shows an initial rise, followed by a definite decrease, as the voltage rises. The reason for the decrease appears to be at least partly the rise in temperature of the film, the efficiency falling as the temperature

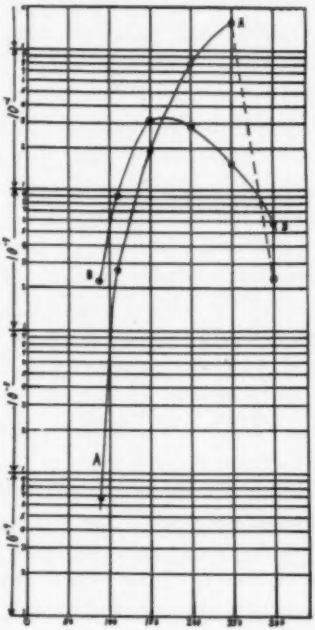

FIG. 1.

FIG. 1. *A, Brightness, and B, Efficiency, as functions of the applied voltage, for 5% solution of $NaHCO_3$. (Cf. Fig. 2.)*

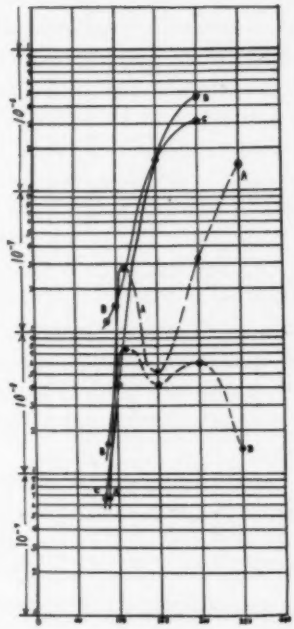

FIG. 2.

FIG. 2. *A, Brightness, B, Efficiency, for 1% solution of $NaHCO_3$, as functions of applied voltage; C, brightness; D, efficiency for 10% solution. (Cf. Fig. 1.)*

approaches the boiling-point of the solution. It is this overheating that prevented extending the curves to higher voltages. The last reading of each run is a "flash" reading (such readings are starred in Table 2), taken within a few seconds after the voltage was applied, no longer time being available before boiling set in. Probably higher efficiencies could be obtained by using water-cooled electrodes.

It might appear that better efficiencies could be obtained by making both electrodes of aluminum, and using alternating current. But the destruction of the film when the current reverses keeps the current which should be suppressed far above the value for maximum efficiency; and while the brightness increases at first with increase of voltage, the efficiency falls steadily.

The accompanying figures will aid in showing the answers to the questions suggested at the beginning of this article. Fig. 1 gives typical curves showing brightness and efficiency as functions of the applied voltage, for 5% solution of sodium bicarbonate. For comparison, Fig. 2 gives corresponding curves for 1% and 10% solutions. An optimum concentration at about 5% is indicated, and tests over the range 0.01% to 20% bear out this conclusion, but show at the same time that the variation with concentration is much less than might have been expected. Similar results have been obtained for other solutions.

Wide variations occur with different chemical solutions, of course, though the few best solutions found give fairly similar results. The ordinates in Figs. 1 and 2 are higher than would be obtained from solutions of sodium carbonate, but not very different from those for the sodium phosphates, shown in Figs. 3, 4, and 5. Contrary to the carbonates, the phosphates show increasing brightness and efficiency as the salts become more basic. Borax solutions would give similar curves.

Impurities generally affect the brightness and the efficiency, but a large number of tests showed that the effects are rarely large enough to be of much importance. It appears impossible to state any general rule regarding the effects of impurities. Some oxidizing agents aided the emission, while others hindered; the same is true of reducing agents. Similarly, no consistent effect was found in making the solution acid or alkaline. It appears likely that impurities in the electrodes themselves might be responsible for certain effects found. The most interesting case of effect of adding an impurity is in the sodium phosphate solutions, especially the di- and tri-basic salts. The effect of adding small amounts of sodium hydroxide is particularly marked at the lower voltages. Thus the addition of 0.6% of NaOH to a 5% Na_2HPO_4 solution reduced the voltage for the threshold of visibility from 80 to 40 volts, and increased the efficiency at 80 volts more than tenfold. The increased brightness persisted to higher voltages, but the increase in efficiency did not. One would expect this impurity only to add a

trace of the more basic salt, to the mono- and di-basic salts; the increase in brightness and efficiency would then be consistent with the fact noted in the preceding paragraph, but would not agree with the fact that a larger amount of the impurity reduced its effect, as was found. The curves for the results are given in Figs. 3, 4, and 5. The concentrations

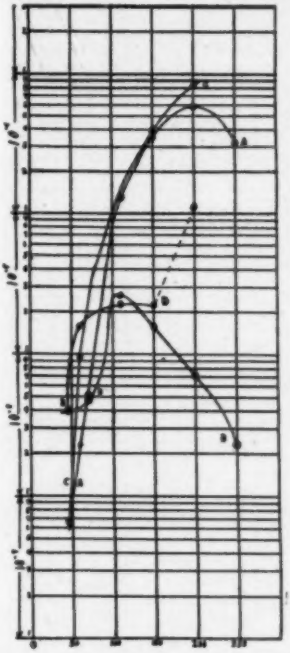

FIG. 3.

FIG. 3. *A, Brightness, B, Efficiency, for a 5% solution of NaH_2PO_4, as functions of applied voltage; C, brightness, D, efficiency, for same solution with .05% NaOH added. (Cf. Figs. 4, 5).*

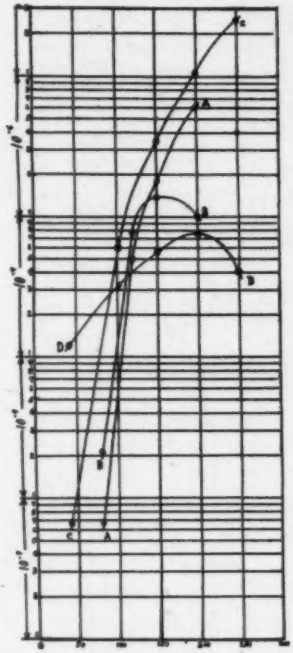

FIG. 4.

FIG. 4. *A, Brightness, B, Efficiency, for a 5% solution of Na_2HPO_4, as functions of applied voltage; C, brightness, D, efficiency, for same solution with 0.6% NaOH added. (Cf. Figs. 3, 5.)*

used were optimum concentrations, as shown by preliminary tests. Additional data are given in Table 2.

It may be objected that sodium hydroxide should not be classed as an ordinary impurity, since of course it changes the p_H of the solution. The effect of making the solution more alkaline has already been referred to. In view of the fact that the luminescence occurs through the wide range of values of p_H from phosphoric acid through the mono- and di-basic salts to the extensively hydrolyzed, strongly basic tri-

sodium phosphate, it seems doubtful to the writer whether the slight changes in p_H due to these small amounts of alkali are sufficient to explain the observed results.

With tantalum electrodes in certain solutions such as dilute sulphuric acid, the film formed shows even higher resistance than those on

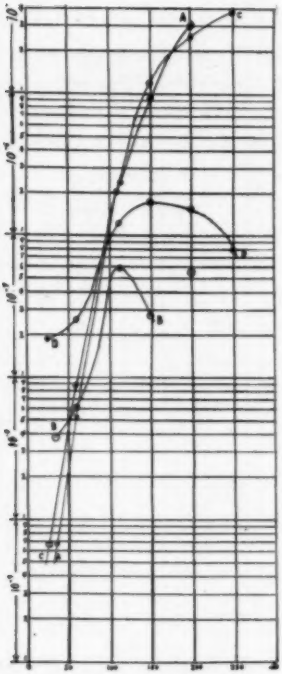

FIG. 5.

FIG. 5. *A, Brightness, B, Efficiency, for 1% solution of Na_3PO_4, as functions of applied voltage; C, brightness, D, efficiency, for same solution with .05% NaOH added. (Cf. Figs. 3, 4.)*

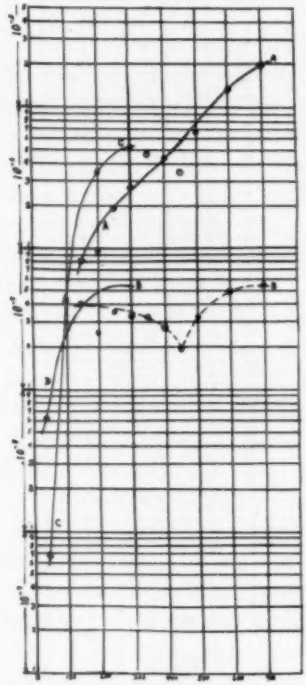

FIG. 6.

FIG. 6. *A, Brightness, B, Efficiency, for upper layer from 1 M solution of p-BrC_6H_4MgBr in anhydrous ether, plotted as functions of applied voltage; C, brightness, D, efficiency, for lower layer of same solution. The corresponding curves for C_6H_5MgBr solution are intermediate between those shown.*

aluminum, so that this metal serves better in rectifiers; this fact is utilized in a commercial patented rectifier. But the brightness and the efficiency of its luminescence are considerably below those for aluminum. Typical values are included in Table 2.

With all the other metals studied in aqueous solutions, the brightness was so low, and the currents so large, that the efficiencies must have been thousands of times less than for aluminum; hence no extended measurements were made.

The Grignard reagents need special mention, for these solutions are in a quite different class from the aqueous solutions previously discussed. The compounds are prepared in absolutely anhydrous ether solutions; they are extremely labile, being quickly attacked by oxygen, and instantly hydrolyzed by water; they react with many other types of compounds.[6] They are characterized by a chemiluminescence on combining with oxygen,[7] which with certain of the compounds is unusually bright. The luminescence during electrolysis does not seem to be closely related to the oxyluminescence, as has been shown.[2] These compounds show a marked Becquerel-effect, a preliminary description of which the writer is at present preparing. The facts regarding the luminescence during electrolysis are interesting. These solutions give brightnesses and efficiencies comparable with those obtained from aqueous solutions. Typical cases are included in Table 2 (c), and shown in Fig. 6. With these solutions, occasionally the light is found at the cathode instead of the anode, and sometimes at both electrodes. It was noticed that in some cases the glow did not start until the voltage had been raised above a certain critical value, at which the light appeared suddenly; it then would persist to lower voltages. It is usually possible to use higher voltages with such solutions than with aqueous solutions. Under proper conditions, the light from a test-tube cell containing one of these substances can be obtained continuously for days. The efficiencies here measured are undoubtedly far below the efficiencies in the bright cases of the oxy-luminescence; for, while the latter have never been measured, it is clear that the luminous output is considerably greater, while the input energy, coming only from the small heat of chemical oxidation, must be very much less than in the present case.

[6] C. J. West and H. Gilman, Organomagnesium Compounds in Synthetic Chemistry, Circ. Natl. Res. Council, no. 24, 1922.

[7] Evans and Dufford, J. Am. Chem. Soc., *45*, p. 278; 1923; Dufford, Calvert, and Nightingale, J. Am. Chem. Soc., *45*, p. 2058; 1923; J. Opt. Soc. Am., *9*, p. 405; 1924; J. Am. Chem. Soc., *47*, p. 95; 1925; Evans and Diepenhorst, J. Am. Chem. Soc., *48*, p. 715; 1926; Dufford, Nightingale, and Gaddum, J. Am. Chem. Soc., *49*, p. 1858; 1927; Dufford, J. Am. Chem.Soc. *50*, p. 1822; 1928.

SUMMARY

1. Luminescence during electrolysis is found to be fairly widespread; typical cases are listed. Good examples are aluminum anodes in sodium phosphate or bicarbonate solutions, or metals in ether solutions of Grignard reagents.

2. The brightness observed in this luminescence ranges from the threshold of visibility to above 10^{-5} lamberts; it increases rapidly with the applied voltage until the heating of the emitting film causes it to fall with further rise in voltage.

3. The efficiency found for this luminescence ranges from 10^{-8} to about 5×10^{-6} %; it behaves qualitatively like the brightness, at first rising, then decreasing, with the applied voltage.

4. Differences in concentration produce relatively small changes in brightness and efficiency, though optimum concentrations seem to exist.

5. The effects with chemically similar solutions are comparable.

6. Impurities generally have a small effect on the brightness and on the efficiency; the most interesting case found, that of traces of sodium hydroxide in sodium phosphate solutions, with aluminum anodes, is illustrated for several cases.

This work was done at the Research Laboratory, Incandescent Lamp Department of General Electric Co., Nela Park, Cleveland, Ohio. The writer takes pleasure in expressing his gratitude to Director W. E. Forsythe, Dr. E. Q. Adams, and the other members of the staff, who made it possible to carry out the work under unusually pleasant circumstances.

PHYSICS DEPARTMENT,
UNIVERSITY OF MISSOURI,
COLUMBIA, MISSOURI.

SOME EXPERIMENTS WITH BINOCULAR AND MONOCULAR VISION*

By E. M. Lowry

From the standpoint of tone reproduction the sensitometric characteristics of the human eye are of primary importance. Consideration of the factors which govern our judgment of distance and form leads to the conclusion that brightness and brightness contrast are certainly the most important of those reproducible by the photographic process.

Attempts to apply the available data on the brightness sensibility of the retina to problems of photographic tone reproduction have shown that these data are entirely inadequate, particularly with reference to the projection of pictures in motion picture theaters. There has been considerable discussion of the conditions which should exist if the best reproduction is to be secured but there appears to be little correlation between the extant data on the discrimination functions of the eye and the brightness relations between the various parts of the finished picture. One of the factors which is probably responsible for the discrepancy between theory and practice is that by far the greater part of the experimental work done has been with monocular rather than binocular perception and in a large number of cases with some sort of optical system or artificial pupil between the eye and the visual field. It seemed advisable for that reason to repeat some of the previous work simulating as nearly as possible those conditions under which the visual processes are normally accustomed to function, that is, using binocular vision and the natural pupil.

There are several features which must be embodied in any apparatus to be used in the determination of the brightness characteristics of the eye if those data are to be applied in practice. In the first place as large an area of the retina as possible should be brought to a definite condition of adaptation. The apparatus used should be so designed that there will be no optical system of any sort between the eyes and the visual field. Further, arrangements should be made so that binocular as well as monocular vision may be used.

As the sensitizing field, a hemispherical bowl (*B*), one meter in diameter, coated on the inside with a matte white paint was provided.

* Communication No. 380 from the Kodak Research Laboratories.

This bowl had a conical-shaped cover (K) in the center of which was a window for the observer's eyes. The cover not only increases the

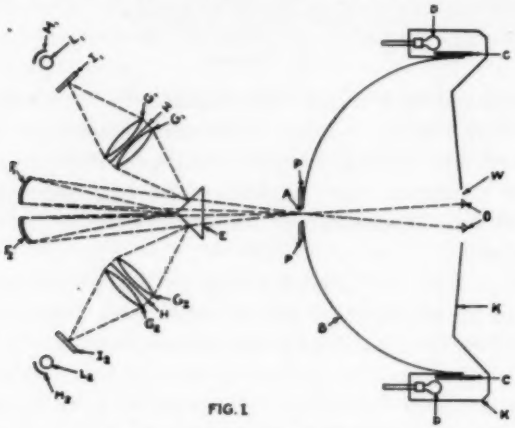

FIG. 1. *Plan of visual sensitometer.*

uniformity of the sphere illumination but also, because of its shape, increases the effective area of the sensitizing field. A ring of lamps (D) furnishes the illumination of the field, the intensity of this illumination being controlled by an annular shutter (C). The shutter is operated

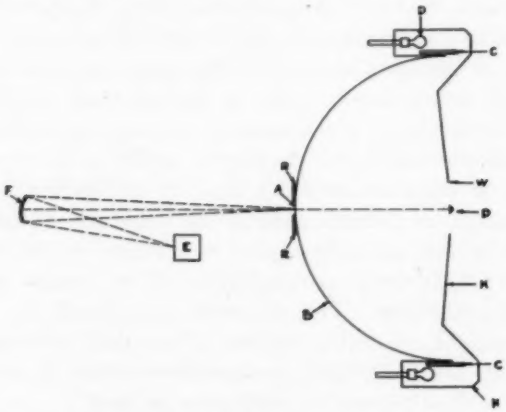

FIG. 2. *Side elevation of visual sensitometer.*

in such a way that the width of the aperture between the edge of the bowl and the cover of the apparatus may be adjusted by the operator

to provide any desired field brightness, within the range of the apparatus, that is, up to 600 millilamberts. At the center of the bowl an aperture (A) serves as the test field. Suitable diaphragms (P) are provided so that the test spot may be made to subtend angles of from fifty minutes to three and one-half degrees at the eyes of the observer. Throughout the work so far with one exception, the smallest aperture (50 min.) has been used to insure strictly foveal vision.

The test field is comprised of aerial images of an alabaster prism E formed at A by the concave spherical mirrors F_1 and F_2. There were two reasons for the adoption of aerial images of the prism for the test field rather than the prism itself. In the first place the formation

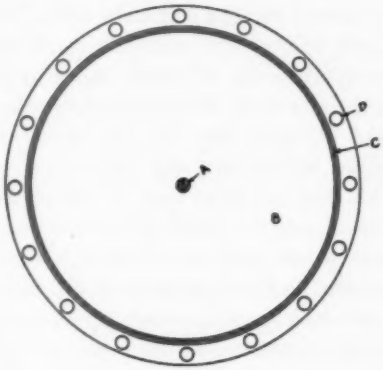

FIG. 3

FIG. 3. *Front elevation of visual sensitometer.*

of the images at A eliminated any parallax that might otherwise have occurred; and second, it enabled the prism, and consequently the test field, to be entirely shielded from any possibility of stray light affecting its brightness.

The illumination of the test field is secured in the following manner: At L_1 and L_2 are lamps which illuminate the fine ground white optical glass disks I_1 and I_2. Behind the lamps are concave spherical mirrors M_1, M_2 for the purpose of increasing the illumination of the disks. The lens systems G_1G_1 and G_2G_2 image the ground glass upon the alabaster prism (E). The intensity of illumination of the faces of the prism is controlled by means of adjustable sector diaphragms H placed between the lenses so that they will be operating in a collimated beam

of light. This type of diaphragm has been described in a paper by L. A. Jones.[1]

At F_1 and F_2 are concave spherical stellite mirrors which form slightly enlarged images of the prism (E) at the aperture A. The image formed by F_1 is seen by the left eye of the observer and that formed by F_2 is seen by the right eye. The appearance of the test field is very similar to that of any ordinary two-part photometer field, such as for example is used in the Martens polarization photometer. The brightness of the two halves of the field is adjustable at the will of the operator by means of knurled heads and shafts connected to the sector diaphragms, the mechanism of which is not shown.

The manner of making a series of measurements is deserving of some attention. A period of approximately fifteen minutes was spent in explaining to each subject the construction of the apparatus and the purpose of the experiments. Although the room in which the work was done was not entirely dark the illumination was subdued and the pre-exposure period allowed time for the effects of previous light exposure to disappear. The subject was seated on a stool whose height, with that of the chin rest and head rest, was so adjusted that his eyes could look comfortably into the observation window. The field illumination was then turned on and three minutes were allowed for the eyes to become adapted to the brightness of the field surrounding the test spot. The three-minute adaptation period was adopted on the basis of Lohman's investigations on the course of light adaptation in which he found that the process proceeds but very slowly following the first two minutes' exposure.[2]

CONTRAST SENSIBILITY

The first work undertaken was a determination of the contrast sensibility of the retina as observed by both binocular and monocular vision. In the observations on contrast sensibility, sometimes referred to as differential or photometric sensibility, the subject was allowed to adapt his eyes, for the three-minute period mentioned above, to the brightness level at which the determination was to be made. At the end of the adaptation period the observer was asked to adjust the brightness of one half of the test field until it was just perceptibly brighter than the other. The series was begun with the test spot illumination just a little above the threshold. The settings of the

[1] J.O.S.A. & R.S.I., *7*, p. 234; 1923.
[2] ZS. Sinnesphysiol, *41*, p. 290; 1906–07.

sector scales were noted and the process repeated until the brightness of the test field had been increased step by step up to or above that of the sensitizing field.

When the observations were to be made with monocular vision, one eye was shielded from the test spot with an opaque mask held in place

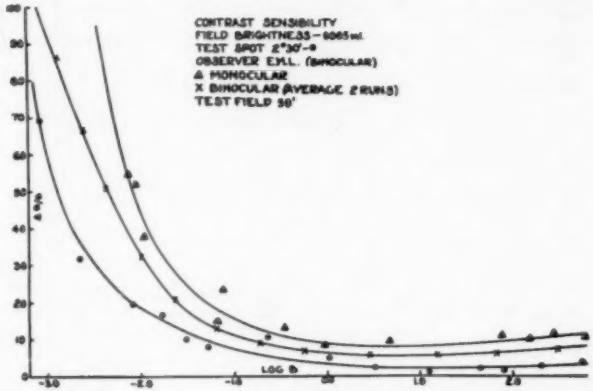

FIG. 4.

by means of a spectacle frame. In this way the eye remained open and did not become dark adapted although it had no part in the judgment of brightness difference.

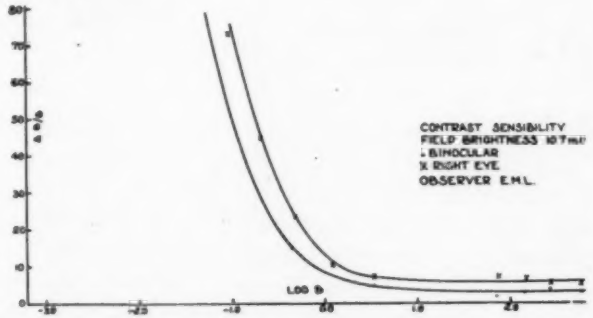

FIG. 5.

The results secured for brightnesses of 0.0005, 10, 50, and 100 millilamberts for both monocular and binocular vision are shown plotted in Figs. 4 to 8 and Tables 1 and 2. The results are in the form of the so-called Fechner Fraction, $\Delta B/B$, where B represents the brightness

of the brighter field and ΔB is the difference in brightness between the two which is first perceptible. In this work the values of $\Delta B/B$ are expressed in per cent.

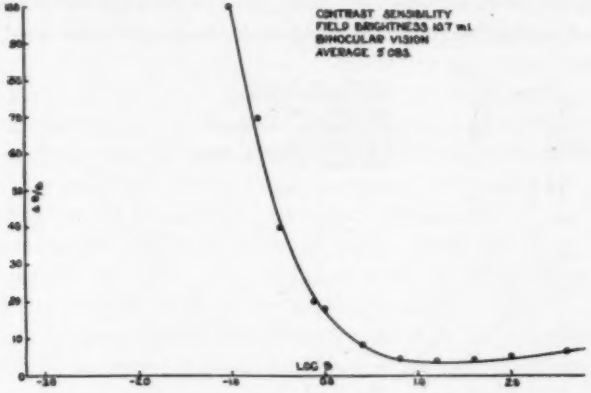

FIG. 6.

A part of the determinations were made by the discontinuous method; that is, the brightness of the test field was set by an assistant and the subject then adjusted one half of the field for a just perceptible difference in brightness from the other half.

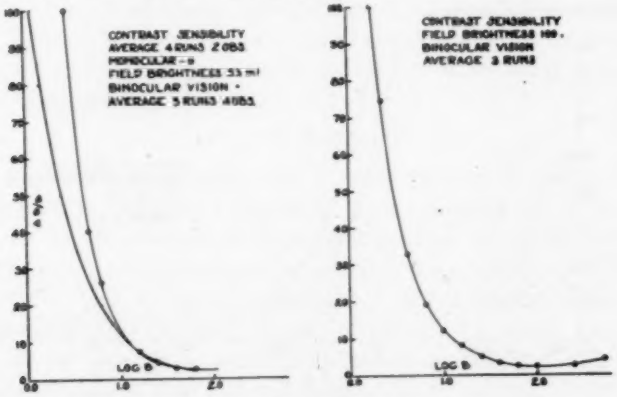

FIG. 7.

Table 1 shows the data for a field brightness of approximately 0.0005 ml which has been plotted in Fig. 4. At the point of maximum contrast sensibility it will be seen that there is a difference of approxi-

mately 45 per cent in the threshold value between binocular and monocular vision. As lower brightnesses of the test field are approached the difference in sensibility between the two methods of observation becomes more marked. The curve for binocular perception is the average of two determinations made on different days. The value for the differential threshold at the position of maximum sensibility for binocular observation is 0.055, a value considerably higher than that usually

TABLE 1. *Contrast sensibility*

Sensitizing field brightness

0.0005 ml (50′ Test field)				0.0005 ml (2°30′ Test field)	
Monocular		Binocular		Binocular	
Log B	ΔB/B	Log B	ΔB/B	Log B	ΔB/B
−3.85	54.9	−3.10	86.4	−4.92	69.3
−3.93	51.8	−3.37	66.5	−3.34	31.8
−2.02	37.7	−3.61	50.8	−3.91	19.7
−2.81	14.9	−2.00	32.3	−2.22	16.6
−2.86	23.2	−2.35	20.7	−2.48	10.0
−1.53	12.8	−2.81	12.5	−2.71	7.8
−1.97	8.0	−1.25	8.7	−1.38	10.5
0.66	9.4	−1.73	6.5	0.02	4.8
1.88	10.5	0.44	5.5	0.52	2.1
2.18	9.9	1.17	5.3	1.10	0.8
2.44	11.2	1.80	5.8	1.66	1.9
2.78	10.3	2.46	7.0	1.90	1.2
				2.31	2.4
				2.77	3.5

assumed. It seemed probable that the discrepancy might well be caused by the use of strictly foveal vision for the determination. The relation between contrast sensibility and the size of the stimulus has been well demonstrated by Reeves.[3] Since it is customary in photometric work to use a field subtending approximately three degrees at the eye, a second run at the same field brightness was made with a diaphragm subtending 2° 30′ at the eye replacing the smaller aperture. The data in this case show a minimum value for the threshold of two per cent which is in accordance with the usually accepted value of contrast sensibility.

At a field brightness of 10.7 ml the threshold for monocular perception has been reduced to about 5.5 per cent and for binocular to

[3] J.O.S.A. & R.S.I., *1*, pp. 148–54; 1917.

about 3 per cent of the brightness of the test field. Table 2 and Fig. 5 show the results for one observer and Fig. 6 the average for five observers.

TABLE 2. *Contrast sensibility*

Sensitizing field brightness

10.7 ml						53 ml				100 ml	
Monocular		Binocular		Binocular Av. 3 obs.		Monocular Av. 4 runs 2 obs.		Binocular Av. 5 runs 4 obs.		Binocular Av. 3 runs	
Log B	ΔB/B	Log B	ΔB/B	Log B	ΔB/B	Log B	ΔB/B	Log B	ΔB/B	Log B	ΔBΔB
−2.97	73.4	−2.85	70.7	−2.99	100.0	0.45	100.0	0.08	100.0	0.24	100.0
−1.30	44.8	−1.17	37.0	−1.29	70.0	0.67	40.0	0.17	80.0	0.36	74.5
−1.68	23.4	−1.64	14.7	−1.52	40.0	0.80	26.0	0.39	50.0	0.62	32.8
0.08	10.3	0.00	8.1	−1.88	20.0	1.00	11.8	0.80	20.0	0.81	19.0
0.53	7.0	0.52	4.8	0.00	17.9	1.20	7.3	0.92	15.0	0.99	12.0
1.87	7.0	1.85	1.5	0.40	8.3	1.40	4.3	1.09	10.0	1.20	8.0
2.17	6.4	2.15	2.8	0.80	4.1	1.60	2.9	1.20	8.0	1.40	5.0
2.43	5.2	2.42	3.7	1.20	3.8	1.80	2.6	1.38	5.0	1.60	3.3
2.77	5.0	2.76	2.7	1.60	4.1			1.60	3.0	1.80	2.5
				2.00	4.9					2.00	2.3
				2.60	6.4					2.40	2.5
										2.73	4.3

In Table 2 and Fig. 7 are data for fifty and one hundred millilamberts field brightness. At these levels the contrast sensibility has

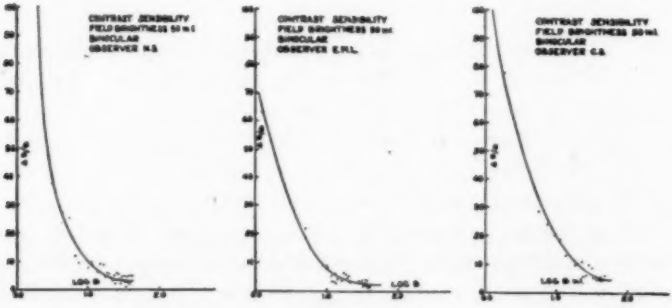

FIG. 8.

apparently reached a maximum as it is practically the same for both. At fifty millilamberts both binocular and monocular vision have very

nearly the same value of sensibility at the maximum although they are still considerably different at the lower brightnesses of the test field. All of the results indicate that at brightnesses below 50 ml there is a marked difference in brightness sensibility between monocular and binocular vision. Fig. 8 has been inserted to show the type of results secured with the step by step method for a few of the subjects.

ADAPTATION

A large amount of work has been done by numerous observers concerning the state of adaptation of the eye in both the scoptopic and photopic conditions. So far as the author has been able to determine, however, the method of measuring the condition of light adaptation has been to adapt the eye to a given brightness and then to determine its sensitiveness immediately after extinguishing the light. While this method surely yields information on the decrease in sensitiveness with light adaptation it does not give the data we are anxious to have, namely, the condition of the retina while it is being stimulated by various brightnesses.

TABLE 3. *Extinction point (in ml)*

Log B Sensitizing field	Monocular Av. 3 runs log Ex. Pt.	Binocular Av. 4 runs Log Ex. Pt.	Binocular Av. 12 runs 5 obs. Log Ex. Pt.
−2.6	−2.03	−3.45	—
−1.0	−2.06	−3.47	−3.71
−1.4	−2.11	−3.57	−3.85
−1.8	−2.20	−3.71	−2.24
0.2	−2.34	−3.90	−2.43
0.6	−2.55	−2.16	−2.67
1.0	−2.84	−2.45	−2.91
1.4	−1.18	−2.81	−1.15
1.8	−1.55	−1.20	−1.31
2.2	−1.96	−1.64	−1.82
2.4	0.18	−1.87	—
2.6	—	—	0.08

In the present series of experiments the point of extinction of light has been chosen as a measure of the adaptation level rather than the threshold. The brightness of the test field at this point may be termed the brightness of black. That is, with the eye adapted for some given brightness, the point at which the illumination of the test field disappears represents the brightness which appears black to the observer.

The procedure followed in adapting the eyes of the subject for the brightness of the field has already been described. Following adaptation the subject was asked to fix his attention on the test spot and to reduce the brightness of first one half of the test field and then of the other until a point was reached at which any further reduction in inten-

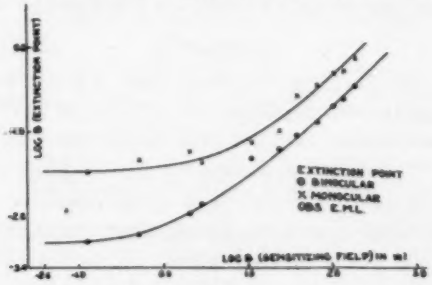

FIG. 9.

sity ceased to produce a deeper black in either portion of the field. The readings of the scales attached to the sectors were noted and the settings repeated several times. The author's eyes were tested both binocularly and monocularly, and although the binocular values are considerably lower than the average of all the observers the results

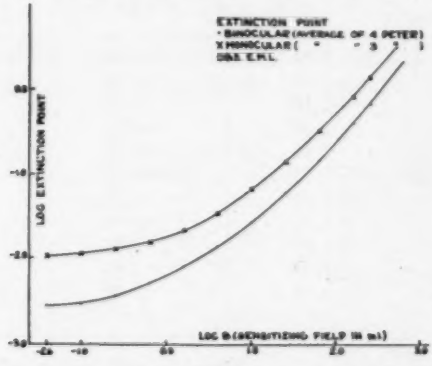

FIG. 10.

show that there is a great difference between the use of one and of two eyes. The monocular results are the average of separate determinations for the right and the left eye.

Fig. 9 shows the values obtained in a single determination and indicates the accuracy of the method. In Fig. 10 the average of four

runs for binocular vision and three for monocular have been plotted. The average of twelve runs for five observers is given in the curve of

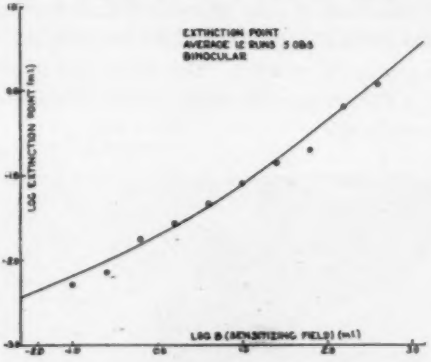

FIG. 11.

Fig. 11. The curves for binocular and monocular observation indicate that while the difference in the extinction point at low brightness is very great, as the adapting field brightness is raised the difference

FIG. 12. *Front view of visual sensitometer.*

becomes less and it is probable that with sufficiently high brightness the values will become very nearly the same.

The brightness of black as determined in these experiments represents the lower limit of the scale of subjective brightnesses necessary for correct interpretation in tone reproduction as applied to the making of the best print from a negative or the best screen reproduction in the case of the projected picture. The other end of the scale, yet to be determined, is the brightness which will best represent white under a given set of conditions.

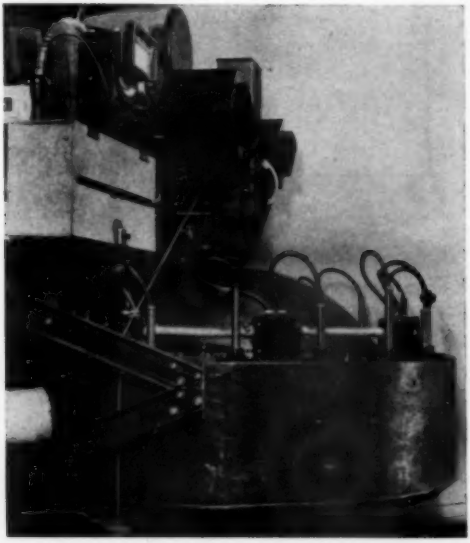

FIG. 13. *Rear view of visual sensitometer.*

The work reported here, while being merely a preliminary study of the brightness sensibility of the human eye as related to tone reproduction problems, indicates without question the necessity of determining the visual characteristics binocularly and with unobstructed vision.

In conclusion I wish to express my thanks to Mr. L. A. Jones for his interest and advice in the work reported here and to those persons who so willingly acted as subjects.

RESEARCH LABORATORY,
EASTMAN KODAK CO.,
ROCHESTER, N. Y.
OCT., 1928.

INSTRUMENT SECTION

A MODIFIED COLORIMETER FOR THE DETERMINATION OF HYDROGEN ION CONCENTRATION*†

By J. J. Beaver

Since the most time-consuming and difficult part of the colorimetric method for the determination of hydrogen-ion[1] concentration is the preparation of the standard buffer solutions much experimental work has been done in recent years on methods which require no standard buffer solutions. These methods depend primarilyupon a knowledge of the dissociation constant of the indicator. If the indicator dissociates as a weak mono-basic acid then the relationship between its dissociation and the hydrogen-ion concentration of the solution can be calculated by means of the equation, $pH = pK + \log \alpha/1-\alpha$, where pK is the "Indicator Constant" and α is the percentage dissociation of the indicator. When the indicator is poly-acidic or poly-basic it does not follow the simple relationship given above and there is no equation that can be used for computing the hydrogen-ion concentration of the solution from the dissociation of the indicator. Therefore, for the present, the colorimetric determination of hydrogen-ion concentration without the use of buffers is limited to one-color indicators and and to those two-color indicators whose dissociations can be calculated by the above equation.

Bjerrum, Michaelis and Sörensen have described methods using one-color indicators, such as the nitro-phenols where it is necessary to determine only the amount of the color. Gillespie[2] describes a method for two-color indicators, where it is necessary to know the concentrations of both the acid and alkaline forms of the indicator. This is accomplished by having each "standard" consist of two tubes, one containing a definite concentration of the acid form of the indicator, the other a known concentration of the alkaline form. These concentrations are so chosen that the sum of the concentrations of indicator in the two tubes is con-

* Contribution from the Department of Chemistry, Columbia University, No. 592.
† Presented at the St. Louis meeting of the American Chemical Society, April 16, 1928.
[1] Clark, W. M., "The Determination of Hydrogen Ions," 2nd edition, pp. 19–26; 1925.
[2] J. Am. Chem. Soc., *42*, p. 742; 1920; Soil Science, *9*, p. 115; 1920.

stant and equal to the concentration of indicator used in the unknown. By changing the ratio of the acid form to the alkaline form standards

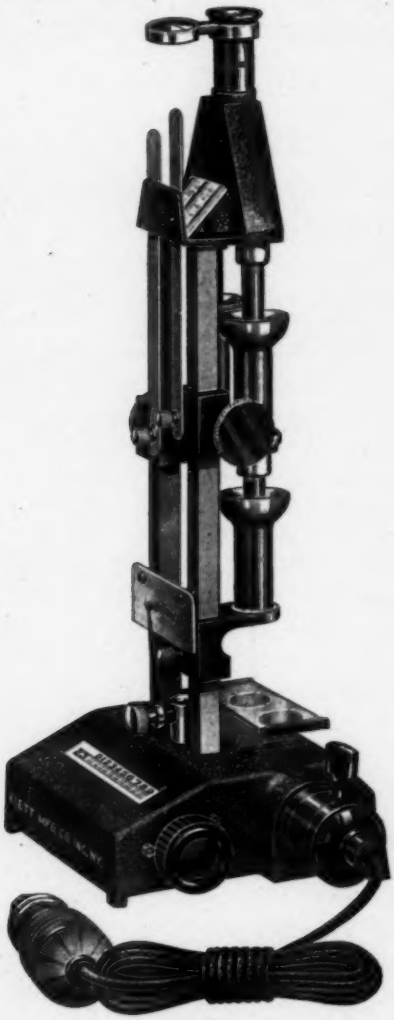

FIG. 1

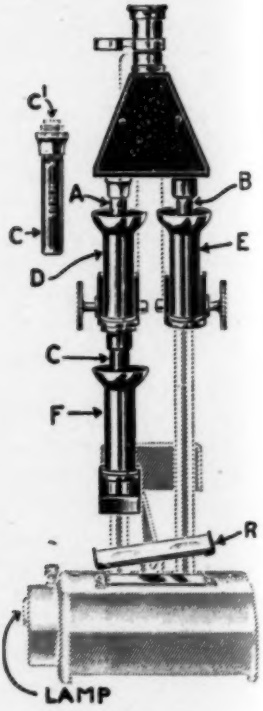

FIG. 2

corresponding to different *pH* values are obtained. This method is more convenient than the usual colorimetric methods but requires

considerable time to make up the standard color tubes. Later Gillespie[3] suggested that much more precise results might be obtained if a special colorimeter were designed for the comparison of the colors. This suggestion was the basis on which the colorimeter described in this article was developed.

After trying several modifications of a Duboscq Type Colorimeter the model[4] shown in Fig. 1 was adopted. This is similar in all respects to a standard colorimeter with the addition of an added cup and plunger. In Fig. 2 is shown a more detailed view of the essential parts of the instrument. In this figure, *A*, *B* and *C* are hollow glass plungers with optically plane and parallel ends attached to the instrument by means of threaded metal adapters. Plungers *A* and *B* screw into the frame of the instrument while *C* screws into the bottom of the holder for cup *D*. This cup holder can be raised or lowered by turning the milled head at the side of the cup. As cup *D* is raised or lowered plunger *C* is also raised or lowered. Cups *D*, *E* and *F* are of black glass on which are fused bases of clear optical glass. The top of each cup is flared to prevent liquid from overflowing even when the plunger is brought in contact with the bottom of the cup. Their diameters are such that with 10 ml of liquid in them a depth of 52 mm can be obtained while 5 ml gives 20 mm depth of liquid.

The holder for cup *F* is held in place by a set screw which can be loosened to permit adjustment of the distance of the cup from the bottom of the instrument. Cup *F* is usually adjusted so that the *total* depth of liquid between the bottom of plunger *A* and cup *D* plus that between the bottoms of plunger *C* and cup *F* is 50 mm. This is easily done by setting cup *D* so that the scale reads 50, which shows that the distance between the plunger *A* and the bottom of the cup is 50 mm, and then bringing up cup *F* until its base is in contact with the face of plunger *C*. Then when cup *D* is raised 10 mm the depth of liquid between its base and plunger *A* is decreased by 10 mm while the distance between plunger *C* and the base of cup *F* is increased by 10 mm. When the amount of unknown solution is small the instrument can be adjusted for some other depth of liquid, say 20 mm, by setting cup *D* at 20 on the scale and raising cup *F* and its holder until stoped by the plunger *C*. This design of instrument keeps the *total* depth of liquid in the light path constant no matter what this total depth or the ratio of the depths of liquid in the two cups may be.[5]

[3] J. Bact. *6*, p. 399; 1921.

[4] This instrument was made by the Klett Manufacturing Company, New York City.

[5] When it is desired to use this instrument as a standard colorimeter plunger *C* and cup *F* are removed.

On the right hand side of the instrument is the cup for the unknown which can be adjusted for any depth of liquid from 1 mm to 50 mm. This depth of liquid is of course, the same as the *total* depth of liquid on the left side of the instrument.

Since the light-ray has to pass through more layers of glass on the left side than on the right side of the instrument the opal glass plate, R, is placed in the light path. By tilting this at the proper angle the light intensities of the two rays can be equalized. This adjustment is very important since with unequal intensities of the two light rays the two half-fields cannot be accurately matched.

In the base of the colorimeter is a metal housing for the 25 watt straight filament electric lamp used as the source of illumination. The light from this lamp passes through a special "daylight" filter before passing through the opal glass equalizer R. The lamp socket is adjustable so that the filament can be properly centered. This light also serves to illuminate the translucent table carried on rollers in the base. This table has the values of the ratio $\log 50-x/x$ from 5 to 45, as well as the pK values, as determined by this instrument, for the common indicators.

If the unknown solution is colored it is necessary to balance this color on the left side of the instrument. This is accomplished by unscrewing C', filling plunger C with the unknown and then screwing C' in place. C' is a short glass plunger fastened to a metal adapter which screws inside the top of plunger C. It is so adjusted that there is just 50 mm of liquid between the bottoms of C' and C. Another short plunger C'' (not shown in the figure) is made which permits a 20 mm depth of liquid between the two plungers. For accurate matching of colors this adjustment is essential, for even the slightest tinge of color or the faintest opalescence makes the matching of colors extremely difficult, if not impossible.

METHOD

In the first method tried 10 ml of distilled water were pipetted into cups D and F and 10 ml of a known buffer solution into cup E. To each cup 5 drops of indicator solution were added and to cup F a drop of molar NaOH and to D a drop of molar HCl. It was soon discovered that this method of producing the standard acid and basic colors of the indicators was not accurately reproducable, so for all the data recorded Hatfield's[6] method was used. He makes four buffer solutions, M acetic

[6] Hatfield, J. Am. Chem. Soc. *45*, p. 940; 1923.

acid, .05M KH_2PO_4, .05M Na_2HPO_4. $12H_2O$ and .01M Na_2CO_3 from C.P. chemicals and uses these to produce the standard colors of the

TABLE 1.

$$P_h = P_k + \log \frac{50-x}{x}$$

Table: $\log \frac{50-x}{x}$

	.0	.1	.2	.3	.4	.5	.6	.7	.8	.9
5	.954	.945	.935	.926	.917	.908	.899	.891	.882	.874
6	.865	.857	.849	.841	.833	.826	.818	.810	.803	.796
7	.788	.781	.774	.767	.760	.753	.747	.740	.733	.727
8	.720	.714	.707	.701	.695	.689	.683	.676	.670	.665
9	.659	.653	.647	.641	.635	.630	.624	.619	.613	.608
10	.602	.597	.591	.586	.581	.575	.570	.566	.560	.555
11	.550	.545	.540	.535	.530	.525	.520	.515	.510	.505
12	.500	.496	.491	.486	.482	.477	.473	.468	.463	.459
13	.454	.450	.445	.441	.436	.432	.428	.423	.419	.415
14	.410	.406	.402	.397	.393	.389	.385	.380	.376	.372
15	.368	.364	.360	.356	.352	.348	.343	.340	.336	.331
16	.327	.323	.319	.316	.312	.309	.304	.300	.296	.292
17	.288	.284	.280	.277	.273	.269	.265	.261	.257	.254
18	.250	.246	.242	.239	.235	.231	.227	.224	.220	.216
19	.213	.209	.205	.202	.198	.194	.191	.187	.183	.180
20	.176	.173	.169	.165	.162	.158	.154	.151	.147	.144
21	.140	.137	.133	.129	.126	.123	.119	.115	.112	.108
22	.105	.101	.098	.094	.091	.087	.084	.080	.077	.073
23	.070	.066	.063	.059	.056	.052	.049	.045	.042	.038
24	.035	.031	.028	.025	.021	.017	.014	.010	.007	.003
25	−.000	−.003	−.007	−.010	−.014	−.017	−.021	−.025	−.028	−.032
26	−.035	−.038	−.042	−.045	−.049	−.052	−.056	−.059	−.063	−.066
27	−.070	−.073	−.077	−.080	−.084	−.087	−.091	−.094	−.098	−.101
28	−.105	−.108	−.112	−.115	−.119	−.123	−.126	−.129	−.133	−.137
29	−.140	−.143	−.147	−.151	−.154	−.158	−.162	−.165	−.169	−.173
30	−.176	−.180	−.183	−.187	−.191	−.194	−.198	−.202	−.205	−.209
31	−.213	−.216	−.220	−.224	−.227	−.231	−.235	−.239	−.242	−.246
32	−.250	−.254	−.257	−.261	−.265	−.269	−.273	−.277	−.280	−.284
33	−.288	−.292	−.296	−.300	−.304	−.309	−.312	−.316	−.319	−.323
34	−.327	−.331	−.336	−.340	−.343	−.348	−.352	−.356	−.360	−.364
35	−.368	−.372	−.376	−.380	−.385	−.389	−.393	−.397	−.402	−.406
36	−.410	−.415	−.419	−.423	−.428	−.432	−.436	−.441	−.445	−.450
37	−.454	−.459	−.463	−.468	−.473	−.477	−.482	−.486	−.491	−.496
38	−.500	−.505	−.510	−.515	−.520	−.525	−.530	−.535	−.540	−.545
39	−.550	−.555	−.560	−.566	−.570	−.575	−.581	−.586	−.591	−.597
40	−.602	−.608	−.613	−.619	−.624	−.630	−.635	−.641	−.647	−.653
41	−.659	−.665	−.670	−.676	−.683	−.689	−.695	−.701	−.707	−.714
42	−.720	−.727	−.733	−.740	−.747	−.753	−.760	−.767	−.774	−.781
43	−.788	−.796	−.803	−.810	−.818	−.826	−.833	−.841	−.849	−.857
44	−.865	−.874	−.882	−.891	−.899	−.908	−.917	−.926	−.935	−.945
45	−.954	−.964	−.974	−.984	−.994	−1.005	−1.015	−1.026	−1.038	−1.049

different indicators. These solutions need not be made up accurately. This method gives far more consistent results than any other tried.

To produce the acid color of thymol blue 0.1M HCl is necessary and was used in all measurements in the acid range of this indicator. Hatfield's observation that the amount of indicator solution could be more accurately measured by counting drops than by trying to pipette in 0.2 ml was verified.

The procedure as finally used was to pipette 10 ml of the proper buffer solution in cups D and F and a like amount of the unknown solution in cup E, each of the cups containing 5 drops of the indicator solution.[7] The volume of the solution and of the indicator should be measured as accurately as possible since the *smallest variation* in the concentration of the indicator in any one of the three cups makes the matching of colors extremely difficult. With cup E set at 50 mm, cup D is moved up and down until the two half-fields match. Since the acid color of the indicator is in cup D the reading x, on the left scale is the amount of acid in the unknown, while $50-x$ is the amount of alkaline color, the total depth of the two colors always being 50 mm. Then from the equation $pH = pK + \log \text{alkaline/acid}$, where $\log \text{alkaline/acid} = \log 50-x/x$, the pH of the solution can be calculated. Table 1 gives the values of $\log 50-x/x$ for values of x from 5 to 45.

TABLE 2. *Indicator constants.*

	pK
Thymol Blue (acid range)	1.70
Brom Phenol Blue	4.10
Methyl Red	(5.00)
Brom Cresol Green	4.86
Brom Cresol Purple	6.07
Brom Thymol Blue	7.08
Phenol Red	7.70
Cresol Red	8.10
Thymol Blue (alkaline range)	8.80
Cresolphthalein	(9.50)

EXPERIMENTAL RESULTS

The indicators given in Table 2 were tested at approximately every $0.2pH$ over their entire ranges using Clark[8] and Lubs buffers, and the constants given are mean values obtained from the data summarized in Table 4. These buffers were checked electrometically with a Leeds and Northrup Type K potentiometer using an Epply Standard Cell

[7] The indicator solutions were made according to the directions of Clark (loc. cit. pp. 80–81). In the case of brom cresol green the directions of Hastings, Sendroy and Robson, J. Biol. Chem. *65*, p. 386; 1925 were followed. The acidic and basic colors of this indicator were produced by N acetic acid and .05M $Na_2HPO_4 \cdot 12H_2O$.

[8] Clark, loc. cit. pp. 99–107.

which was checked against another cell, standardized at the Bureau of Standards, and a saturated calomel electrode. For all buffers except those containing potassium hydrogen phthalate freshly platinized platinum electrodes were used and found to be reproducible to ± 0.0005 *V*. The phthalate buffers always drifted toward the acid range with hydrogen electrodes but remained constant for hours with the quinhydrone electrodes. So the buffers between *pH* 2.2 and *pH* 6.0 were all measured using the quinhydrone electrode, which in turn was checked against the hydrogen electrode by means of 0.1M HCl. Temperature was maintained constant to $25° \pm 1°$ C.

Each colorimetric value is the mean of two separate determinations each of which, in turn, is the mean of 10 settings on the colorimeter. Table 3 is a typical series of readings on the colorimeter while Table 4 gives the results obtained by the two methods. Temperature maintained constant to $25° \pm 1°$ C. in all experiments.

TABLE 3. *Phenol red.*

Reading on Colorimeter
28.0
28.2
28.0
28.0
28.1
28.3
28.0
28.0
28.3
28.1

Mean = $28.09 \pm .11 \rightarrow$ pH = $7.59 \pm .004$.
With hydrogen electrode pH = $7.61 \pm .02$.

In the following table (5) are given the readings obtained with methyl red and cresol phthalein. Neither of these indicators dissociates in the same manner as the others[9] and the following data are given so that the *pH* of a solution may be computed from the reading on the colorimeter.

The above data when plotted fall on smooth curves which have much greater curvature than those of the other indicators. Therefore the constants given in Table 2 for these two indicators are useful only near the mid points of their ranges.

Solutions of various colors, blue, yellow and red, and of known *pH* were tested on the colorimeter. Using the procedure described above the only effect of the added color was to diminish the intensity of the light in both halves of the field. When the added color was too deep no

[9] All indicators were obtained from the same manufacturer.

TABLE 4.

Thymol Blue (Acid Range) pH			Brom Phenol Blue pH		
Colorimetric	Electrometric	Δ	Colorimetric	Electrometric	Δ
*(1.15±.02	1.34	−.19)	2.78±.01	2.81	−.03
1.30±.006	1.32	−.02	3.12±.006	3.15	−.03
1.46±.01	1.48	−.02	3.53±.009	3.50	+.03
1.68±.002	1.68	±.00	3.76±.006	3.73	+.03
1.97±.006	1.96	+.01	3.88±.002	3.87	−.01
2.25±.003	2.27	−.02	4.09±.002	4.08	+.01
2.41±.006	2.38	+.03	4.37±.003	4.35	+.02
2.67±.006	2.64	+.03	*(4.78±.04	4.65	+.13)
2.81±.01	2.81	±.00			
		Av. =.016			Av. =.023

Brom Cresol Green pH			Brom Cresol Purple pH		
Colorimetric	Electrometric	Δ	Colorimetric	Electrometric	Δ
4.00±.011	4.03	−.03	5.14±.006	5.13	+.01
4.32±.008	4.30	+.02	5.38±.009	5.36	+.02
4.68±.007	4.65	+.03	5.56±.003	5.55	+.01
4.91±.007	4.89	+.02	5.91±.003	5.90	+.01
5.04±.006	5.04	±.00	6.26±.006	6.26	±.00
5.14±.003	5.13	+.01	6.44±.003	6.46	−.02
5.29±.004	5.31	−.02	6.60±.005	6.63	−.03
5.53±.006	5.55	−.02	*(6.74±.007	6.80	−.06)
		Av. =.019			Av. =.014

Bromthymol Blue pH			Phenol Red pH		
Colorimetric	Electrometric	Δ	Colorimetric	Electrometric	Δ Z
6.26±.01	6.23	+.03	6.86±.006	6.83	+.03
6.40±.02	6.38	−.02	7.05±.003	7.04	+.01
6.59±.003	6.60	−.01	7.28±.002	7.30	−.02
6.83±.004	6.80	+.03	7.41±.003	7.39	+.02
7.05±.006	7.04	+.01	7.59±.001	7.61	−.02
7.28±.007	7.30	−.02	7.76±.003	7.78	−.02
7.59±.006	7.62	−.03	7.91±.006	7.94	−.03
*(7.71±.01	7.78	−.07)	8.41±.005	8.41	±.00
		Av. =0.21			Av. .019

TABLE 4 (continued.)

Cresol Red pH			Thymol Blue (alkaline range) pH		
Colorimetric	Electrometric	Δ	Colorimetric	Electrometric	Δ
7.42 ± .007	7.39	+.03	7.95 ± .009	7.94	+.01
7.64 ± .001	7.61	+.03	8.15 ± .008	8.10	+.05
7.80 ± .005	7.78	+.02	8.43 ± .006	8.41	+.02
7.97 ± .002	7.94	+.03	8.49 ± .002	8.50	−.01
8.10 ± .002	8.10	±.00	8.73 ± .003	8.76	−.03
8.51 ± .003	8.50	−.01	8.95 ± .003	8.95	+.00
8.77 ± .005	8.76	+.01	9.19 ± .007	9.22	−.03
			9.40 ± .007	9.43	−.03
		Av. = .019	9.56 ± .009	9.54	+.02
					Av. = .022

* These values are not used in computing the averages.

satisfactory matching could be made. But it was found that pineapple juice, lemon juice and tomato juice could be measured with an average deviation of ±.05 *pH*.

TABLE 5.

Methyl Red		Cresol Phthalein	
pH Electrometric	Reading on colorimeter	pH Electrometric	Reading on colorimeter
4.65	43.5	8.53	47.2
4.86	38.8	8.76	43.3
5.04	31.6	8.95	39.5
5.13	25.3	9.22	28.5
5.40	14.0	9.43	17.2
5.55	10.5	9.54	12.0
5.90	4.5	9.78	4.2

CONCLUSION

A modified colorimeter is described for measuring the *pH* of solutions colorimetrically without the use of standardized buffer solutions. The method is rapid and accurate and can be used on colored or turbid solutions if the color is not too deep. Further the instrument can be used as a regular colorimeter by removing the added plunger and cup.

DEPARTMENT OF CHEMISTRY,
COLUMBIA UNIVERSITY,
NEW YORK, N. Y.

CHART OF THE ELECTROMAGNETIC ENERGY RELATIONS

By W. Edwards Deming

The accompanying tabulation and graph were designed to facilitate electromagnetic energy calculations. One is frequently confronted by such simple questions as "What frequency corresponds to an electron having a speed of 500 volts?" or "What is the fractional relativity increase in transverse mass of a body moving with a speed of 2×10^{10} cm sec^{-1}?" These charts will save time in answering such interrogations.

Fig. 1. *Chart of the electromagnetic waves.*

In compiling tables there always arises the consideration of just what and what not to include, and of what form of exposition is best—curves, tabulation, or some clever arrangement of parallel scales. Curves (such as Fig. 2) possess advantages over a discontinuous tabulation like

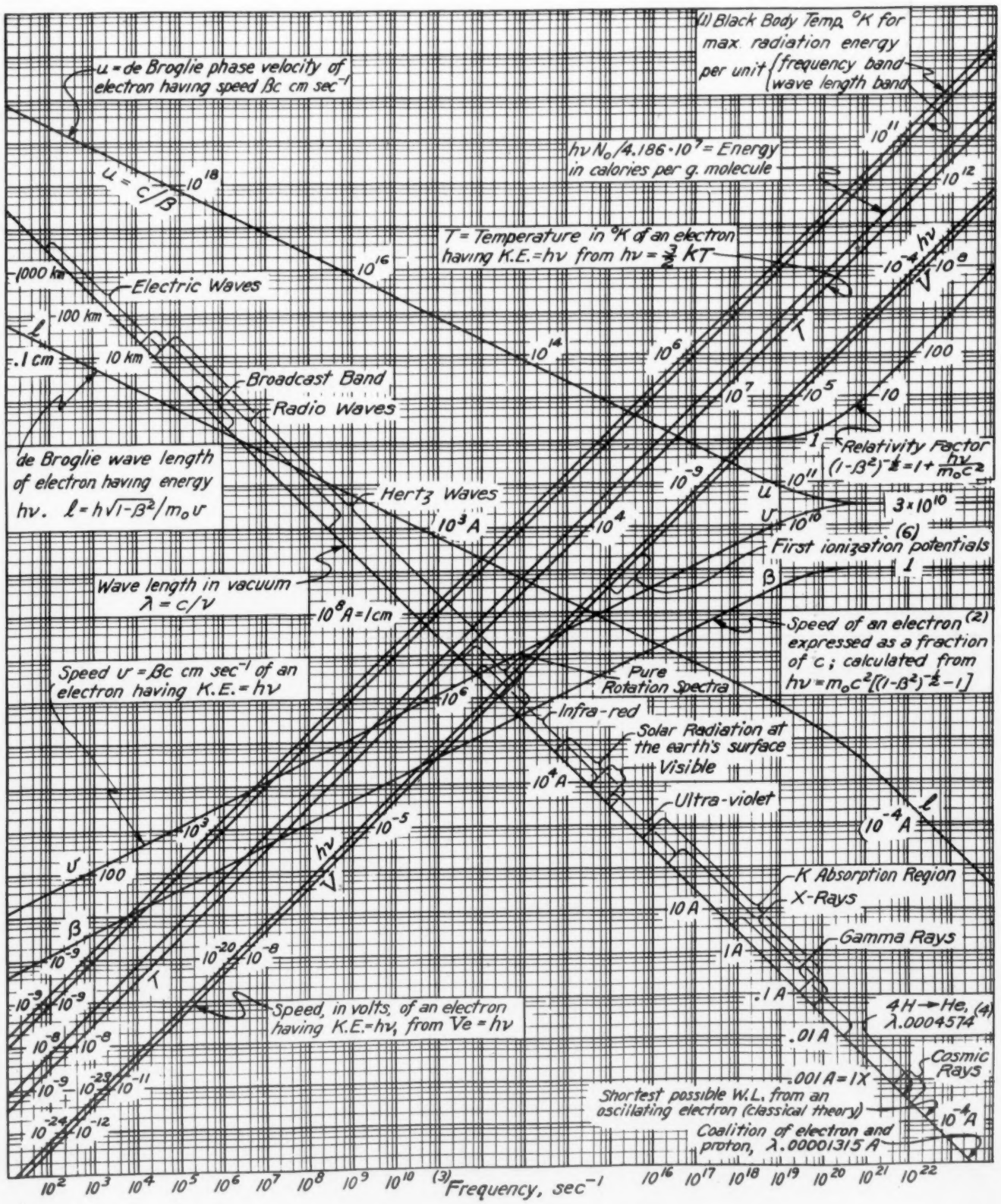
(1) Black Body Temp. °K for max. radiation energy per unit {frequency band / wave length band
u = de Broglie phase velocity of electron having speed βc cm sec⁻¹
hν N₀/4.186·10⁷ = Energy in calories per g. molecule
T = Temperature in °K of an electron having K.E. = hν from hν = 3/2 KT
u = c/β
Electric Waves
1000 km
100 km
10 km
.1 cm
Broadcast Band
Radio Waves
Hertz Waves
de Broglie wave length of electron having energy hν. ℓ = h√(1-β²)/m₀v
Wave length in vacuum λ = c/ν
10⁸A = 1cm
10³A
Relativity Factor (1-β²)^-½ = 1 + hν/m₀c²
3×10¹⁰
(6) First ionization potentials
Speed of an electron (2) expressed as a fraction of c; calculated from hν = m₀c²[(1-β²)^-½ - 1]
Speed v = βc cm sec⁻¹ of an electron having K.E. = hν
Pure Rotation Spectra
Infra-red
Solar Radiation at the earth's surface
Visible
Ultra-violet
10⁴A
(10⁻⁴A
K Absorption Region
X-Rays
10A
1A
.1A
Gamma Rays
4H → He, (4) λ.0004574
.01A
.001A = 1X
Cosmic Rays
Shortest possible W.L. from an oscillating electron (classical theory)
Coalition of electron and proton, λ.00001315A
Speed, in volts, of an electron having K.E. = hν, from Ve = hν
(3) Frequency, sec⁻¹

FIG 2. *Chart of the electromagnetic energy relations.*

Fig. 1, but if a person is anxious for four-figure accuracy at particular points, he can never get it from an ordinary sized graph. So it has seemed advisable to include both curves and tabulation. The curves (Fig. 2) are simply the data of Fig. 1 plotted, and with the de Broglie wave length and velocity added.

The following explanations are all that are needed. The numbers on the figures correspond to the various reference marks.

1. In black body unpolarized radiation the energy transmitted per second per unit frequency band per unit solid angle is, by Planck's radiation formula, $K_\nu = (h\nu^3/c^2)/(e^{h\nu/kT}-1)$; per unit wave-length band it is $E_\lambda = (hc^2/\lambda^5)/(e^{hc/\lambda kT}-1)$. The values $h\nu/kT = 2.82144 \equiv a$ and $hc/\lambda kT = 4.96511 \equiv b$ make K_ν and E_λ take their maximum values, whence the temperature for maximum energy per unit frequency band or per unit wave-length band can easily be computed for any frequency or for any wave length.

2. Electron speed $\div (1846)^{1/2}$ = equivalent speed of an alpha particle, with negligible error at low speeds. This holds to within 0.1% up to $\nu = 3\times10^{17}$, but becomes 1.8% low at $\nu = 3\times10^{18}$, 12% low at $\nu = 3\times10^{19}$, and should not be used at all for higher frequencies. For convenience, $.6968 \div (1846)^{1/2} = .01622$; $20.89 \div (1846)^{1/2} = .4863$; $66.07 \div (1846)^{1/2} = 1.538$; $.2203 \div (1846)^{1/2} = .005129$.

3. In this chart, frequency has been made the fundamental quantity from which everything else is computed, using

Speed of light, $c = 3\times10^{10}$ cm sec^{-1}
Electronic charge, $e = 4.774\times10^{-10}$ esu
Electronic mass, $m_0 = 8.999\times10^{-28}g$
Planck's constant, $h = 6.554\times10^{-27}$ erg sec
Molecular gas constant, $k = 1.372\times10^{-16}$ erg per$^\circ C$
300 volts = one esu of p.d.
One calorie $= 4.186\times10^7$ ergs
Avogadro's number, $N_0 = 6.061\times10^{23}$ mole^{-1}

4. Using at. wts., $H = 1.00778$, $He = 4.00216$

5. This interval separates octaves.

6. Corresponding to "first ionization potentials", Cs 3.88V, He 24.48V, kindly supplied by Dr. F. L. Mohler of the U. S. Bureau of Standards.

Several different vertical scales had to be used in order to get all the curves on the same sheet. The scale for each curve is marked along side of it.

These drawings are the handiwork of Mrs. C. Sherry, draftswoman at this laboratory. Their preparation was undertaken at the suggestion of Dr. F. G. Cottrell, director of this laboratory, who has been a constant source of support. I am also indebted to several other friends, chiefly Dr. A. E. Ruark of Mellon Institute, for their suggestions.

U. S. DEPARTMENT OF AGRICULTURE,
BUREAU OF CHEMISTRY AND SOILS,
WASHINGTON, D. C

Carboloy A new tool material, composed of tungsten carbide and cobalt, has been developed. The material is extremely hard and the cobalt gives it the strength necessary for cutting tools. This hard metal composition will be marketed under the trade name "Carboloy." The material is particularly valuable in the cutting of low-tensile materials which are abrasive to the present type of tool, and in this class of work Carboloy tools have been found to be from 25 to 75 times as durable as high-speed steel tools. It can also machine harder and denser grades of steel than can be handled economically by high-speed steel, machine rods of glass or porcelain, or drill holes in concrete and rock where it was formerly necessary to use either an expensive diamond drill or a star hammer. In a comparative test on molded materials containing metal inserts, such as fabric gears used in automobiles, cobalt chromium alloy cutters, which had given the best previous service in this work, required redressing for every 150 parts machined. Carboloy tools under identical conditions finished 11,000 parts before they required resharpening.

When it came to determining quantitatively the hardness of the new cutter it was found that the usual method of using the Rockwell test could not be used as the point of the diamond wore and crumbled in too short a time if the diamond penetrator was loaded with a weight. It was therefore necessary to use the penetrator without a load. The test showed that common hardened tool steel has an average maximum hardness of 850 on the Brinell scale, that the hardest steel may be taken as about 1000, and that the hardness of Carboloy runs 2000 or better.

The addition of cobalt to the tungsten carbide increases its strength to more than half that of high-speed steel. Tungsten carbide without cobalt has a strength of less than 50,000 pounds per square inch; Carboloy up to 275,000 pounds, and quenched and tempered high-speed steel 425,000 pounds. The material retains its strength and hardness at high temperatures to a remarkable degree, and tools made of it have been observed cutting nickel steel when the point of the tool was at a bright red heat, without showing any ill effects. It has no temper to be drawn by the heat generated.

GENERAL ELECTRIC COMPANY

NOTE ON FILTER RADIOMETRY OF INCANDESCENT LAMPS

By Donald C. Stockbarger, Alexander L. M. Dingee, and Laurence Burns

For a number of years the incandescent tungsten lamp has been used as a source of continuous ultraviolet radiation. Gehlhoff[1], Franck and Grotrian[2], Stockbarger[3], and others, have developed special types of lamps and have shown that when operated at a high filament temperature they are satisfactory for many types of absorption studies. Such lamps are usually fabricated with quartz bulbs or windows. For near ultraviolet work thin soda-lime bulbs can be used successfully, although the intensity in the neighborhood of 3000A is reduced somewhat by absorption.

In particular, from the point of view of convenience, the automobile headlight lamp is proving itself useful in the laboratory. When the filament temperature is raised to about 3400° K, under which condition its length of life is but a few hours, the ultraviolet emission to 2900A is easily detected on the fluorescent screen of a Hilger quartz spectroscope. As illustrated by Fig. 1, the spectrum can be photographed below that point without greatly over-exposing the visible region.

Radiometric studies were begun in the summer of 1927 to determine the percentage of total radiant energy in several arbitrary spectral regions in the ultraviolet. These determinations were made by means of a thermopile and galvanometer with glass filters for making the spectral separations. Work of this kind is sufficiently straightforward that fairly precise numerical data can be obtained by studying a large number of lamps. The principal difficulty lies in interpreting the data for it is not evident what spectral limits should be assigned to each section measured. The effective cut-off of a filter cannot be the point at which the transmission curve meets the zero axis, nor the one at which the transmission first reaches the maximum value. It depends on the energy distribution of the source and therefore that must be known before the cut-off can be determined.

[1] Gehlhoff, G., Über eine konstante Lichtquelle mit kontinuierlichem ultraviolettem Spektrum. ZS. f. techn. Physik, *1*, p. 224; 1920.

[2] Franck, J. and Grotrian, W., Über die Absorptionsbanden von Quecksilberdampf. ZS. f. tech. Physik, *3*, p. 195; 1922.

[3] Stockbarger, D. C., An Incandescent Lamp with a Quartz Window, J.O.S.A. & R.S.I., *9* p. 337; 1924.

The main purpose of this paper is to present a method of finding filter cut-offs for use when dealing with continuous radiation. Not knowing the energy distribution of the incandescent lamp radiation, we have had to assume it to be that of a black body. The spectral limits, calculated on this assumption, have been used in interpreting some of the incandescent lamp data previously obtained. It is to be emphasized that the assumption of black body conditions had nothing to do with the radiation measurements. It merely made possible the assignment of much more nearly correct spectral limits than would otherwise have been possible.

The same spectral limits were applied to the black body radiation curve, and the energies between them computed, to determine roughly whether or not Planck's law held in the ultraviolet region for incandescent tungsten radiation.

FIG. 1. *Spectrograms obtained using automobile headlight type incandescent lamps operated far above normal input. Top, lead glass bulb; middle, soda-lime glass bulb; bottom, Vitaglass bulb.*

In making the radiation measurements, the following filters were employed: crown glass No.1, crown glass No. 2, noviol 0 glass and quartz water cell (1 cm). The spectral limits of the first three as determined by the method outlined below, were 3170, 3330 and 4200A, respectively. The cut-off of the water cell was assumed to be 14000A. This assumption was without effect on the ultraviolet analyses.

With the source at a convenient distance from the thermopile, which had a crystal quartz window, galvanometer readings were taken with (a) no filter, (b) water cell, (c) water cell and noviol 0, (d) water cell and crown No.1, (e) water cell and crown No. 2, and (f) water cell and crystal quartz (or thin Helioglass) between the source and thermopile. The ratio of (b) to (a) corrected for transmission and reflection losses in the water cell was the fraction of the radiant energy having wave lengths less than about 14000A. The method of estimating the correct-

ion to be applied to a reading was the same in each case and consisted in taking the ratio of deflection with two identical filters in the path of the radiation to that with one filter in place. In determining the correction factor for any of the glasses, the water cell was in position constantly.

The corrected ratio of (f) to (b) was found to be slightly less than unity, which indicated that in our apparatus some reflection errors were present. Therefore, to determine the fraction of the energy below 3170A present in the spectral band terminating at 14000A, the corrected ratio

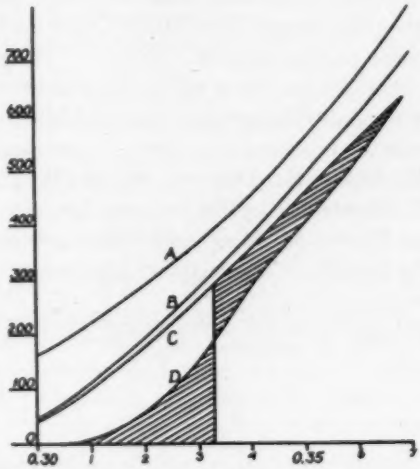

FIG. 2. *A, energy distribution of black body radiation; B, energy distribution of the same radiation after transmission through thin soda-lime glass; C, same as B, except that all ordinates have been multiplied by 0.92, the maximum transmission of the filter; D, same as B, except that all ordinates have been multiplied by the respective transmissions of the filters. Ordinates, E_λ. Abscissas, wave length in microns.*

of (d) to (b) was subtracted from the corrected ratio (f) to (b) instead of unity. Ordinarily this procedure would be unnecessary, but in this case the fraction sought was of the same order of magnitude as the reflection error.

The corrected value of (f) was nearly the same whether quartz or thin Helioglass was employed. The fractions of the energy below 3330 and 4200A, present in the same band, were found by subtracting the ratios (e) to (b) and (c) to (b), respectively, from the ratio (f) to (b), all ratios having been corrected. To translate the values in terms of total radia-

tion instead of the band terminating at 14000A, the figures were multiplied by the corrected ratio of (b) to (a).

To determine the effective spectral limits of the filters the following method was employed. First it was assumed that the radiation approximated that of a black body in accordance with curve *A* of Fig. 2. To obtain curve *B* for the radiation after transmission through the soda-lime bulb, the ordinates were multiplied by the respective transmissions of this glass. The ordinates of the latter curve were then multiplied by 0.92, the maximum transmission of the filter, giving curve *C*; and multiplied by the respective transmissions of the filter, giving curve *D*. Curve *D* represents the energy distribution of the radiation reaching the thermopile after passing through the filter. The problem was to find by trial the wave length below which the transmitted energy was equal to that lost above by absorption. The method therefore consisted in balancing two errors resulting from the fact that the filter transmission curve was not rectangular in shape. Adding the energy discarded below the cut-off, represented by the left crosshatching, to the energy transmitted above the cut-off gave in effect a rectangular transmission curve terminating sharply at the arbitrary abscissa.

TABLE 1. *Observed and calculated values of spectral energy distribution of radiation from small incandescent tungsten lamps.*

	Observed	Calculated
< 3170*A*	0.046%	0.014%
< 3330*A*	0.11 %	0.04 %
< 4200*A*	0.55 %	— %
<14000*A*	57 %	— %

In the above table are given the percentages of total radiation found using a large number of automobile headlight lamps with soda-lime bulbs. In each of the first two regions the observed value was approximately three times the calculated value. The latter was obtained by calculating the ratio of energy below the wave length in question to that below 4200A, and multiplying by 0.55 percent.

It must be admitted that such figures, based as they are on the differences between large and nearly equal quantities, cannot boast of extreme accuracy. Being the average values obtained from observations made on a number of lamps, and being of the same order of magnitude as a large number of other figures which were discarded for experi-

mental reasons, we venture to suggest that the high percentages of ultraviolet are due to selective emission.

A little consideration of the method employed in determining spectral limits will show that our assumption of black body conditions was conservative and that the high percentages are not due to that. If we had assumed a law more favorable to the ultraviolet region, the limits would have been lower, and consequently a still higher percentage of energy in a given region would have been found.

ROGERS LABORATORY OF PHYSICS,
RADIATION MEASUREMENTS DIVISION.
MASSACHUSSETTS INSTITUTE OF TECHNOLOGY,
CAMBRIDGE, MASS. SEPTEMBER 14, 1928.

Anomalous Dispersion in Thallium Vapor. The use of Haken method of anomalous dispersion of thallium vapor was measured in the neighborhood of the lines 3776 and 5330. It was found that the relative value of the number of, dispersion centers for these lines changes with the temperature according to Boltzmann's law, as follows:

$$N_{3776} : N_{5350} = ae^{-(E_1 - E_2)/kT}$$

where E_1 and E_2 are the energies of states 6^2P_{12} and 6^2P_{32}. The probabilities of the spontaneous transition $2s \rightarrow 2p_1$ and $2s \rightarrow 2p_2$ are equal, that is, $A_{2s \rightarrow 2p_1} : A_{2s \rightarrow 2p_2} = 1$. W. K. Prokofjew and W. N. Solovjew, Trans. Opt. Inst. Leningrad, *4*, No. 41, 41 pp.; 1928. (In Russian).

The Standardization of the Weber Photometer. The scale of an ordinary Weber photometer was tested in which the deviation of illumination of the milk-glass plate from the theoretical value of J/R^2 was determined. A formula is developed for the correction coefficient to take care of the reflection on the inside walls of the photometer. The theoretical curve was in complete agreement with the experimental data. The reflection coefficients of the inside walls of the photometer are tabulated in tables and curves. Lydia Djomkina, Trans. Opt. Inst. Leningrad, *4*, No. 42, 9 pp.; 1928. (In Russian).

A VACUUM-TUBE CIRCUIT FOR MEASURING SMALL ALTERNATING CURRENTS

By R. Earl Martin

The problem of measuring alternating currents below the range of the ordinary thermo-galvanometer is quite often a serious one. The apparatus required is very expensive, the range of frequencies which a given device will measure is quite often limited, and the sensitiveness is not always that to be desired. Having met with some of the above mentioned difficulties, the following described arrangement was devised in an effort to eliminate them.

Four vacuum tubes, type UX201 – A, and a D'Arsonval galvanometer were connected in a circuit as shown in Fig. 1. These tubes are so arranged that for each direction of the emf in the external circuit the current will pass in the same direction through the galvanometer. It may be seen that when the electron current is from the right it will pass upward through tube 1, downward through the galvanometer, upward through tube 3 and out onto the line. If the electron current is from the

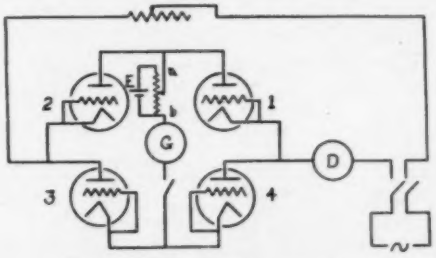

Fig. 1. *Sketch of electrical connections.*

left it will pass in a similar manner through tube 2, the galvanometer and tube 4. The battery E is placed in the circuit as shown to prevent a flow of current through the galvanometer due to the electrons given off by the heated filaments even though no outside voltage is impressed on the system. To adjust the value of this emf so that it will just prevent a flow of current through the galvanometer when no external emf is applied, the sliding contact a is moved toward b until a deflection occurs and then moved away from b until this deflection is just reduced to zero. With this condition existing any external emf whatever should cause a current to flow through the galvanometer. Since in the circuit

the filaments of tubes 3 and 4 are already connected they may be heated by the same battery. However, tubes 1 and 2 must be heated by independent batteries. The grids are all connected to their respective filaments.

By means of a circuit such as is described above alternating currents as small as the corresponding direct currents to which the galvanometer will respond can be measured. As long as the frequency is not over a few thousand cycles per second no corrections need be applied to the observations. However, for high frequencies the tubes are not perfect rectifiers, but due to the capacity afforded by their electrodes they pass some current in each direction. A correction must be applied to the observations when the frequency of the impressed emf is very high.

Fig. 2, is a sketch of the equivalent circuit for Fig. 1, at the instant the current is from right to left. For this direction of flow, tubes 1 and 3 function as a condenser and a resistance in parallel, while tubes 2 and 4 function as only condensers. During the next half cycle the parts played by these two sets of tubes will be interchanged. Since the current through the galvanometer is unidirectional it may be represented by a pure resistance. The inductance of the galvanometer serves to keep the current through it steady and the instrument indicates the average current passed by it.

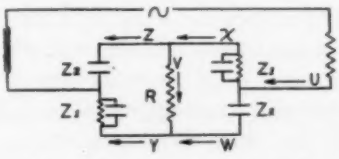

FIG. 2. *Equivalent electrical circuit.*

Applying Kirchoff's laws to the different elements of this circuit we obtain the following equations.

$$v + z = x \tag{1}$$

$$v + w = y \tag{2}$$

$$x + w = u \tag{3}$$

$$Z_1 x + Rv - Z_2 w = 0 \tag{4}$$

$$Z_1 y + Rv - Z_2 z = 0 \tag{5}$$

where u, v, w, x, y, and z represent currents as shown in the figure. $Z_1 = r/(1+\omega^2 C^2 r^2)^{1/2} =$ and $Z_2 = 1/\omega C$, where $\omega = 2\pi$ times the frequency,

r = the effective plate to filament resistance of one of the tubes and C the plate to grid capacity. Solving these equations for u in terms of v we obtain.

$$u = \frac{2R + Z_2 + Z_1}{Z_2 - Z_1} v.$$

To test this relationship a Duddell thermo-galvanometer, D, was placed in the circuit as shown in Fig. 1. This galvanometer had previously been calibrated. Since the deflections of this instrument depend upon the heat generated in a heater coil placed near a thermo-junction it is evident that due to the "skin effect" the resistance of this heater will increase with the frequency and thus cause deflections larger than would be produced by the same currents at a lower frequency. However since this heating element is a straight conductor of uniform sectional area, it is easy to compute the rise in resistance due to the "skin effect" at any frequency. The deflections may then be corrected accordingly.

Beginning with a 60 cycle ac taken from the power mains, then using current from an audio frequency generator whose range could be varied from 100 cycles to 10000 cycles, and finally using current from a radio frequency generator whose range was from 100 000 to 3 000 000 cycles corresponding readings of the D'Arsonval and Duddell galvanometers were taken. The deflections of the D'Arsonval galvanometer are a measure of the average current passed by it while the deflections of the Duddell galvanometer are a measure of the root-mean-square current passed by it. In order to compare the readings of the two instruments this fact must be given consideration. Since, no matter what the shape of the alternating current wave is, it can always be resolved into some number of sine or cosine waves, and whatever is true for one of these sine waves is true for all of the sine waves. Let us consider a representative wave given by the relation

$$i = I_0 \sin \omega t$$

The average value of i during a half cycle is $2I_0/\pi$, and since all of the impulses given to the D'Arsonval galvanometer are in the same direction the deflection produced will be same as for a direct current equal to $2I_0/\pi$. Also the root-mean-square value of i during any half cycle is $I_0/\sqrt{2}$ and the indications of the Duddell galvanometer will be the same as for a direct current equal to $I_0/\sqrt{2}$. Hence the current as indicated by the D'Arsonval galvanometer will have to be multiplied by

the ratio of these values, $\pi/2\sqrt{2}$, before comparing it with the current indicated by the Duddell galvanometer. Fig. 3 shows a plot of a typical set of data obtained in this manner.

In computing the correction to be made for the current passed by the tubes due to their capacitance, the value of both r and C were measured in the laboratory and the values found to agree quite satisfactorily with those furnished by the manufacturer. For UX201-A tubes these values are $r = 12000$ ohms and $C = 7.97$ micro-microfards.

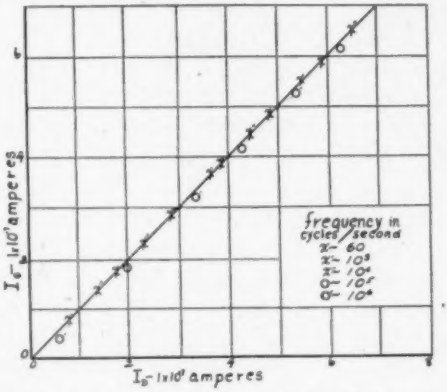

FIG. 3. *Showing accuracy of device for measuring small alternating currents.*

The line plotted in Fig. 3 is the line upon which all the points would lie if the two instruments checked with one another. The low frequency points all fall approximately on this line while those for the higher frequencies would fall on a line parallel to the one plotted but slightly displaced from it. This deviation is perhaps due to a variation of the characteristics of the tubes from one another or from that as measured. This calibration of the arrangement is only carried down to the currents of the order of 10^{-7} amperes. This was due to limitations imposed by the Duddell galvanometer. As used in my work currents of the order of 10^{-9} amperes have been measured. The arrangement will measure these currents at low frequencies accurately and at high frequencies the error will be only a few percent, when the proper corrections are made even though the calibration is carried out at low frequencies and for relatively high currents.

PHYSICAL LABORATORY,
LEHIGH UNIVERSITY,
BETHLEHEM, PA., SEPTEMBER 15, 1928.

A SUBLIMATION MERCURY STILL*

By K. Hickman

A laboratory still for the purification of mercury which would appear to perform excellently has recently been described by Booth and Jones.[1] It has the advantage that it is constructed of standard iron pipes and fittings and that it requires no attention in working. In comparison the still which is now to be detailed is a delicate piece of glassware but it combines with refinement a reliability which will appeal to those using quantities of pure mercury. It was evolved to aid the development and maintenance of some self-recording vacuum gauges to be described elsewhere.[2] So much mercury became soiled day by day in these experiments that it was convenient to have a still into which the soiled fluid could be poured for immediate repurification.

It is agreed with Hulett,[3] Bettel,[4] and others that chemical treatment before distillation is absolutely essential for the removal of metallic impurities. If, however, the distillation is performed in *a sufficient number of stages*,[5] small quantities of foreign metal may accumulate in the first stage residue without contaminating the final effluent. This postpones the troublesome washing with acid to infrequent occasions.

The failure of some distillation operations to secure purification is due to splashes of mother liquor being carried over with the vapor into the distillate. It was, therefore, decided to use vacuum distillation, or rather sublimation into a vacuum space which would allow no boiling nor ebullition to disturb the liquid surface. The nucleus of the idea was obtained from the excellent apparatus set up for the purification of thermometer mercury by the Taylor Instrument Company. Here, after the suggestion of Prof. Moler,[6] a wide glass tube some 35 inches long terminating in a closed bulb is inverted over a narrower tube of double the length. The inner tube passes through the bottom of a trough which supports the outer tube and also contains the mercury to be distilled. At its lower extremity the inner tube bends over,

* Communication No. 369 from the Kodak Research Laboratories.

[1] Ind. & Eng. Chem., *19*, p. 104; 1927.

[2] J. O. S. A. and R. S. I.

[3] Phys. Rev., *21*, p. 388; 1905.

[4] Chem. News, *97*, p. 158; 1908.

[5] G. A. Hulett, Phys. Rev., *33*, p. 307; 1911.

[6] Private communication from Cornell University.

making a syphon trap before it discharges into a receiving bottle. Fig. 1 shows the apparatus, clamped in position and filled for working. Mercury has been placed both in the trough, *A*, and in the bend, *B*, and suction has been applied by the narrow glass tube, *C*. After the liquid has reached barometric height, the gas flame has been started at the ring, *D*, and the residual gases boiled out. *C* was then broken at the bend below the liquid, leaving the still ready for operation. So long as the burner is kept alight and the trough contains mercury, the liquid rises above the flame level and distillation takes place.

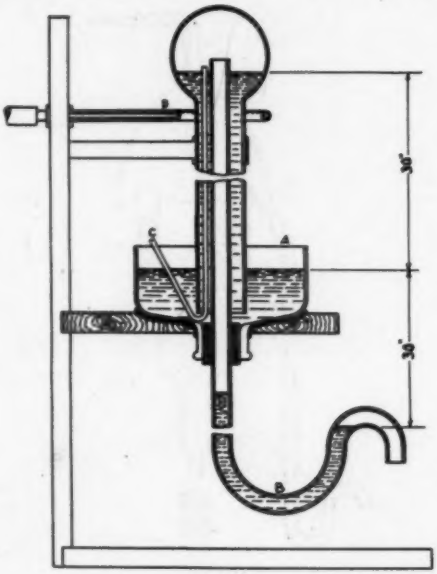

FIG. 1.

For our purposes this excellent apparatus had some minor drawbacks:

1. The use of a gas heater with naked flame was objectionable in our laboratory.

2. An electric heater consumed too much energy because the heat was applied externally where the loss was great; while the condensation was accomplished internally, where the cooling was relatively poor.

3. The units were not easily coupled to give series distillation. The mercury became exposed to air and dirt contamination while transferring from one still to the next.

4. Refilling and re-evacuating involved dismantling the apparatus.

During trial experiments with this type of still it was noticed that if insufficient heat were supplied by the gas burner, most of the mercury vapor condensed on the upper part of the bulb and ran down the sides so that it had again to be vaporized. Only the vapor in excess of that needed for this action actually passed down the inner tube for final condensation. It was felt that a more efficient form of still unit could be made, utilizing this bulb condensation for yielding the pure mercury. Accordingly, a bulb was blown in the form of an alembic of shape and dimensions shown in Fig. 2, and mounted about 32 inches

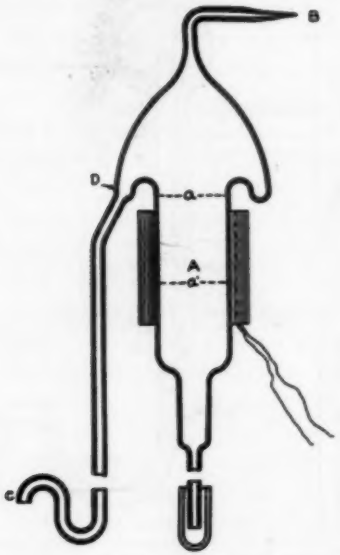

FIG. 2.

above a glass dish. Mercury placed in the dish could be drawn up into *A* by applying suction at *B*, provided that sufficient mercury had been introduced at *C* to seal the bend. If now, *A* was heated, mercury vapor passed directly from the surface of the mercury to the walls of the alembic, where it condensed and fell down into the annulus. To accomplish the heating electrically two layers of asbestos paper were wrapped around *A* and this was then wound with 45 inches of nichrome resistance wire (10 ohms per meter). A further wrapping with asbestos paper for electrical and heat insulation completed the heating unit.

During use the level of mercury in A fluctuated from a to a' according to the outside atmospheric pressure and the depth of liquid in the dish. Shortly after turning on the current (31 volts from a toy ac transformer), droplets of mercury condensed on the walls of the alembic and collected in the annulus D whence they flowed by way of C into a collecting bottle.

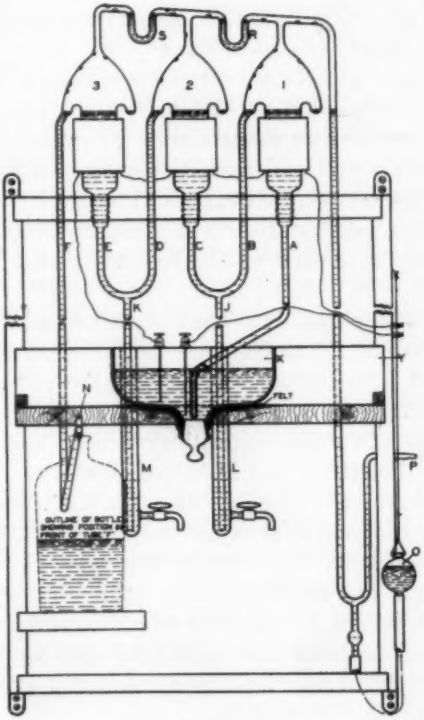

FIG. 3.

It soon became evident that the scheme would produce sufficient mercury (about 400 cc in 24 hours) for our purpose, without variations of pressure and level interfering. An automatic still was therefore constructed with three of these units in series.

In Fig. 3 is shown the complete arrangement. The three alembics, wound with resistance wire in a manner described later, are mounted on a hard wood board. This board forms the top member of the wooden

framework and is pierced with seven holes[7] through which the alembic tubes have been pushed during assembly. If the elementary design were followed these tubes would all be carried to the shelf below, the one marked *A* ending in the supply trough *X*, while *B* and *C*, *D* and *E* dipped into two separate test tubes, and *F* delivered the pure product to a waiting bottle. It is manifestly better, however, to join *D* to *E* and B to *C* just below the alembic, and carry two tubes, *J*, *K*, to the base. Were is not for the necessity of occasionally cleaning the apparatus, even these could be omitted.

The first alembic receives mercury from a shallow trough *X*, which is made conveniently from the top half of a glass-stoppered bottle turned upside down. This shape allows the collecting tube to reach into a little central pool and remain submerged when the trough is substantially empty. A welded steel box with a depression at one corner would do equally well but glass was preferred for ease in cleaning. The bottle is held on a shelf which allows the neck to pass through a central hole.

At the back of the shelf is a wooden strut situated directly under the row of alembics. Through holes in this strut two narrow test tubes, *L* and *M*, 8 inches long and one-half an inch in diameter, are pushed from below. About 1½ inches from the bottom of each test tube there is sealed in a side tube with stop cock. This allows mercury to be drained out of the second and third alembics to below the junctions with the drop tubes *J* and *K*, while the still is running, and thus disposes of any contamination which may have distilled over during some months' operation. The final outflow tube, *F*, from alembic 3, is carried through the lower wood strut and bent in the form of a double *U*, or horizontal *S*, with vent pipe, *N*, on the last bend, such that the final outflow takes place under the shelf supporting the feed trough. A small shelf below this pipe accommodates a receiving bottle in a position virtually free from dust.

In the top of the alembic it will be noticed that there is a much contorted connecting tube prolonged from No. 1 to reach down to the base of the wood stand where it terminates in a long Y-piece. The lower limb of the Y is furnished with a piece of rubber pressure tubing about 40 inches long terminating with a small mercury reservoir bulb *O*. The side limb *P* is left open except when connected with the exhaustion pump. The side tube should be 25 inches below the

[7] The function of the seventh tube will be described later.

alembic bulbs, while the bottom limb should reach to 36 inches below. The reservoir should be tied so that the mercury surface is about 33 inches below the bulbs.

The action of the still will be apparent from the following description of the method of putting it into operation. Well washed mercury is poured into the trough, *X*, the reservoir, *O*, the test tubes, *L* and *M*, and the bend in *F*, through vent, *N*. The reservoir, *O*, is then lowered until it rests about 65 inches below the alembics and then the side tube, *P*, is connected to an oil pump (a "Hyvac" pump answers excellently). The pump is run for a few turns after which it will be found that the mercury has mounted a part of the way up the vertical tubes. The test tubes and the U-bend are then replenished if necessary, so that the pumping may be continued until the alembics are full. The electric current is now turned on with, of course, the pump still running and when there are signs of mercury distilling, the bends *R* and *S* are warmed with a Bunsen or alcohol flame to prevent condensation. After distillation has been proceeding vigorously for about half an hour, it is assumed that all residual gases have been driven off, enabling the Bunsen flame to be withdrawn. In a few minutes mercury condenses, filling the bends *R* and *S*, and seals each alembic from its neighbor. The rubber tube connecting the apparatus with the pump is now clipped as near as possible to the glass side tube, *P*. The mercury reservoir *O* is raised to its normal position. This sends a column of mercury up both limbs of the *Y* exhaustion tube and seals the apparatus completely from the outside air. The joint between the glassware and the rubber tube leading to the reservoir is thus subjected to mercury above atmospheric pressure and leaves no possibility for inward leakage of air. The clip between the apparatus and the pump being kept closed, the rubber tube is slipped off allowing the mercury in *P* to subside to a level below the alembics corresponding with barometric height.

At this stage the test tubes are full of mercury which may have no claim to special cleanliness. The stop cocks are therefore opened and the mercury drained out of alembics 2 and 3 and transferred to the feed trough. In the course of an hour or two the alembics will become filled by distillation from No. 1 and then from No. 2, allowing quite pure mercury to pass to the final receiver.

For the still to run well it is important that the electric winding and the asbestos lagging be placed accurately. Commerical asbestos

paper is cut into strips 2 inches wide, and a short length sufficient to give exactly two convolutions is placed around the glass stem. On the top of this is wound exactly 50 inches (measured as effective heating length and disregarding thicker lead-in portions) of nichrome wire having a resistance of 10 ohms per meter. This is for alembic 1. Nos. 2 and 3 have 54 inches each, the proportions insuring that the first distillate never exceeds the capacity of the second and third stills. The windings are now covered with eight layers of paper and are tied neatly in place. The whole winding and insulation operation is best done before the long fall tubes have been sealed on and before the alembics are mounted in the woodwork. The three windings are afterwards connected in series and are run without added resistance from the 110-volt house mains. It has been found convenient to include in the circuit two steel rods which dip into the feed trough to within 1 mm of the bottom. This enables the trough to be filled up before leaving in the evening with the assurance that the receiver will be full of clean mercury in the morning, and that the still will have been shut off automatically when the supply of crude mercury became exhausted. Those who object to the house circuit passing through the mercury will find it easy to include a simple relay.

The cleaning of the glassware before the first filling is not difficult. Although it would be best to aspirate in order: chromic acid, water, caustic soda, and distilled water, through the entire assemblage and follow this by a stream of warm air, it has been found sufficient to clean the alembics only in this manner before assembling. If, then, the boiling out during evacuation is performed thoroughly, and the first two or three days' distillate is rejected, rewashed, and replaced in the trough, a very pure product finally becomes available.

The most convenient place to keep the still is in a corner of the room hanging on the wall. The alembic should be about six feet above the floor so that the reservoir may be lowered when needed. The wooden framework has been designed without back or front for some of the glass blowing operations to be done *in situ*. Pyrex only is to be used and the receiving bottle should be of similar material, never of lead glass.

The still has a capacity of about 400 cc in 24 hours, equal to about 12 liters a month in constant use. This will meet the requirements of most laboratories.

EASTMAN KODAK RESEARCH LABORATORY,
ROCHESTER, N. Y.,
JULY 31, 1928.

A STILL FOR LIQUIDS OF HIGH BOILING POINT*

By K. Hickman

To aid the distillation under reduced pressure of unstable organic liquids it is customary to draw air or other gas through the apparatus. This prevents bumping and increases the yield of distillate by reducing the partial pressure. There are, however, some liquids so difficult to handle that the admission of air causes oxidation or else raises the boiling point until decomposition occurs.

Such difficulties were suffered acutely when trying to distill certain high boiling liquids which have been found useful in lubricating the mercury meniscus against the glass of manometer and barometer tubes and other vacuum apparatus.[1] Among other compounds, butyl phthallate, butyl stearate, and methyl oleate have been found excellent in this respect, but only when pure. Ordinary vacuum distillation with an air stream yields distillates sufficiently acid to attack mercury on long standing. A different method had, therefore, to be devised.

It is well known that distillation will take place rapidly under extremely low pressures if the evaporating and condensing surfaces are large enough and sufficiently close together. Bronstead and Hevesey[2] fractionated mercury successfully at little above room temperature. The vacuum was the highest attainable and the condensing surface was then less than the mean free path of the mercury molecules away from the liquid surface. Recently Dr. Washburn has announced, at the Swampscott meeting of the American Chemical Society,[3] the distillation under excessively low pressures of such apparently non-volatile solids as sucrose.

Unfortunately an exactly similar procedure is not applicable to crude organic liquids because volatile impurities prevent the necessary reduction in pressure. Experiments with a sublimation mercury still, however, described elsewhere in this issue suggested that a still made in the form of an alembic might allow the surface of the liquid under treatment to be brought so near the condensing surface that distillation would occur rapidly under pressures much lower than usually employed in organic laboratories.

* Communication No. 368 from the Kodak Research Laboratories.

[1] To be published elsewhere.

[2] Phil. Mag. *43*, p. 31; 1922.

[3] Sept., 1928; proceedings not yet published.

Consequently an electrically warmed vessel was constructed in which the surface of the liquid undergoing distillation could be within a centimeter or so of the cooling space. A preliminary test was made distilling some liquids which ordinarily decompose when boiled. A yellow sample of methyl oleate, for instance, volatilized without apparent boiling and condensed to a colorless liquid at the rate of 5 cc a minute under a vacuum of 1/50 mm of mercury (secured by a "Hyvac" pump).

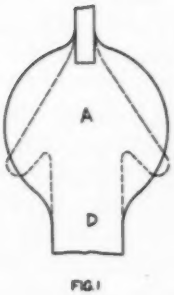

FIG. 1

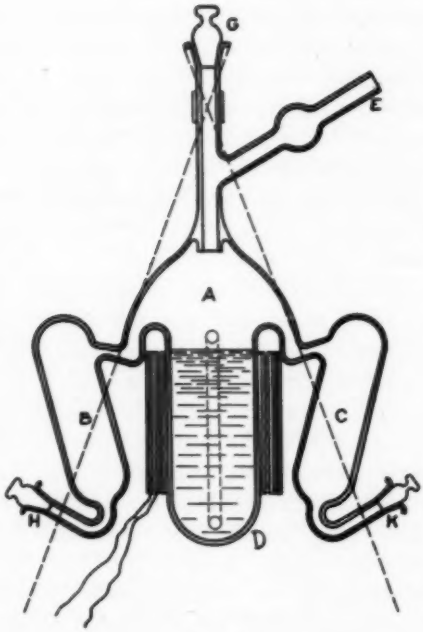

FIG. 2.

The apparatus was simplified for every day use in the laboratory, and provision was made for collecting more than one sample of distillate. The method of construction is apparent from Fig. 1, while Fig. 2 shows a section of the finished apparatus. A bulb *A*, 3 inches in diameter is blown from a pyrex glass tube *D* of about 1½-inch bore, and a tube 3/8-inch in diameter is sealed into the top to project internally by half an inch. The bulb is then tapered and the base pushed in to yield an alembic. Two or three side reservoirs *B* and *C*, etc., one inch diameter and two inches long are sealed to the annular channel

of *A* and the tube *D* is closed at the bottom. It is convenient to provide *B* and *C* with stoppers.

The 3/8-inch tube entering *A* is fitted with a stopper also and a side tube with a small bulb, *E*, is sealed on. A strip of asbestos paper 2 inches wide is wrapped twice around *D* and secured in place by a winding of nichrome wire to serve as a heating coil. Forty inches with a resistance of 10 ohms per meter is convenient. The winding is covered with four layers more of the asbestos paper and the whole is kept in position with a few turns of wire. The heating coil is connected with a toy ac transformer, or to a dc resistance such that a current varying between 1/2 ampere and 3 amperes may be passed through.

In operation the stopper, *G*, which, of course may be replaced by a thermometer, is temporarily removed while the liquid is poured into *D* to a level not exceeding that shown (Fig. 1). *E* is now connected to the vacuum pump which is operated for 10 or 15 minutes before any heat is applied. This frees the liquid from dissolved air. If this precaution is not taken, the slightest warming produces an explosive evolution of bubbles and vapor which splashes the liquid into the receivers. In fact, some liquids contain so much dissolved air or volatile matter that bumping cannot be avoided. This led Mr. C. R. Sanford, of this laboratory, to make the valuable suggestion of adding a waste tube (shown by dotted lines in the figure) to connect the rim of the alembic with the bottom of the main bulb. The unit, which is clamped by the neck in a retort clamp can then be tipped so that all splashes fall into the rim and down the return tube to the main body of liquid. When bubbling ceases, the current is turned on and the alembic left in position until steady distillation is taking place. It is then so twisted that one of the receivers is lowermost and a preliminary fraction collected. When sufficient distillate has come over, the angle is altered and a second and perhaps third portion is isolated. Finally the vacuum is released and the fractions are taken from their reservoirs by loosening the stoppers. It is interesting to notice that with low enough pressures only the part of the condenser opposite the mouth of the bulb becomes hot, the annulus region in the shadow receiving little of the rarefied gas stream.

If the apparatus is used carefully, there is absolutely no danger of contaminating the pump oil. Where traces of volatile solvents have to be removed first, a small condenser standing in ice and salt should be placed between the alembic and the pump.

EASTMAN KODAK RESEARCH LABORATORY,
ROCHESTER, N. Y.

AN AUTOMATIC MERCURY STILL

By F. L. Robeson

ABSTRACT

A new form of vacuum mercury still is described. This still is easily made from standard laboratory glassware, starts and stops automatically, and needs very little attention. The power required is 90 watts for an output of 100 grams of mercury per hour.

The chemical method of purifying mercury by allowing a stream of fine drops to fall through a long tube of the reagent is tedious and unsatisfactory. Hulett's method* of distillation with the admission of a fine jet of air to the still in which a partial vacuum is maintained by a pump in continuous operation, is an unnecessary refinement except where the highest degree of purity is required. The vacuum still here illustrated was constructed by the writer several years ago and has proved most satisfactory. It is a modernization of the design of Prof. Smith of Oxford, employing two barometric columns to maintain the vacuum.

This still can be made easily by any one who has had a little experience at glass blowing. It is entirely of pyrex. The boiler *B* is an ordinary round bottom or water bottle flask of 200 ml capacity. It is sealed into the bottom of an Erlenmeyer flask *C* of 100 ml capacity, which forms the condenser. A ring is heated around the joint between the two flasks and the bottom of *C* is pressed up slightly to form the groove *GG*. Dents *D'D''* are made in opposite sides of the neck with a triangular file, extending to the center of the tube, to prevent particles from being blown directly into the condenser by a bursting bubble.

The supply tube *F* and discharge tube *J* are of 4 mm inside diameter. *F* should be of a length equal to the average barometric height at the locality where the still is used. *J* terminates in the trap *T*, and its length from the top of the trap to the shoulder should be about 3 cm greater than average barometric height.

The heating coil *HH* of chromel wire conforms to the bottom of the boiler and is covered with alundum cement. The circuit is completed with two iron wires extending nearly to the bottom of the steel supply cup *S*. If the wires are adjusted so that the circuit breaks on both sides at the same time, as the mercury goes down in the cup, the arcing is reduced. The coil takes 1.88 amperes at 48 volts. A small auto-trans-

* G. A. Hulett, Phys. Rev., *33*, 307; 1911.

former from a discarded arc lamp is used to step down the 110 service voltage.

To start the still the first time after cleaning, an air pump is connected to the discharge tube J by a short piece of rubber tubing carrying a pinchcock. The mercury to be distilled is washed free of grease and

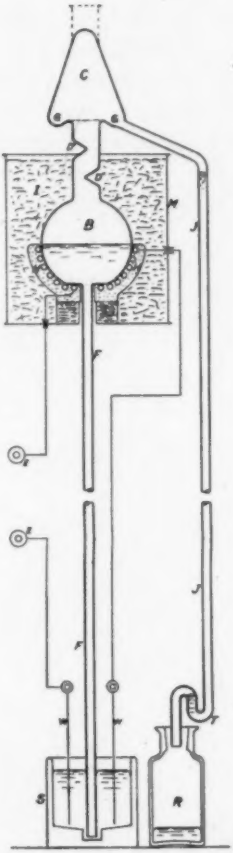

FIG. 1. *Mercury still*

poured into S. This closes the heating circuit. The pump is started and the mercury rises into the boiler. The pinchcock is then closed until drops of distilled mercury have nearly sealed the trap T. The pump is then set going again, the pinchcock opened, and the pumping

continued until sufficient mercury has come over to seal the outlet securely. The pinchcock is then closed again and left closed until mercury has collected to slightly more than barometric height in the tube *J*. The pinchcock is then opened, the rubber tube removed; and the still is operating under a vacuum of approximately 1 cm of mercury if a good pump has been used.

After the two barometric columns have been established to maintain the vacuum, the still is started by merely pouring mercury into the cup *S*. It stops when the mercury gets below the points of the iron wires. The amount of mercury needed to keep the still sealed is 45 ml, and the energy required is about 1 kilowatt-hour per kilogram of mercury distilled. With ordinary use in our laboratory of four hundred students, the boiler needs to be washed out with nitric acid about once a year.

PHYSICS LABORATORY,
VIRGINIA POLYTECHNIC INSTITUTE,
BLACKSBURG, VA., NOVEMBER, 1928.